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RESEARCH ON SYNTHESIS PROCEDURES FOR INTERMEDIATES REQUIRED FOR HIGH TEMPERATURE STABLE POLYMERIC MATERIALS

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Midwest Research Institute

TECHNICAL REPORT AFML-TR-69-326, Part II

June 1971

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FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-69-C-1351, "Research on Synthesis Procedures for Intermediates Required for High Temperature Stable Polymeric Materials." The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. George Moore (LNP), as Project Scientist.

This technical report covers the work conducted from 15 October 1969 to 15 April 1971. The manuscript was released by the authors in May 1971 for publication as a technical report.

The work was carried out by Mr. R. N. Clark, Mr. G. L. Whittier, Mr. L. W. Breed, and Dr. C. W. Kruse with Dr. C. C. Chappelow, Jr., as Principal Investigator for Midwest Research Institute during most of the report period; Dr. Chappelow prepared this report.

This technical report has been reviewed and is approved.

R. L. VAN DEUSEN
Chief, Polymer Branch
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ABSTRACT

Work on the synthesis of the following substances is reported: Benzidine 3,3'-dicarboxylic acid, 6,6'-bis-([4*H*],3,1-benzoxazine-2,4-[1*H*]-dione), diethyl 2,5-diaminoterephthalate, pentafluorophenylphosphonous dibromide, bis(pentafluorophenyl)phosphinous bromide, perfluoro-1-bromo-4-*n*-octylbenzene, 1,1'-bis(formyl)ferrocene, 1,3-bis(phenylglyoxaloyl) benzene, pyracyloquinone, and *p*,*p*'-oxydibenzil. Work on the characterization of the following compounds is reported: 1,1'-bis(formyl)ferrocene, ruthenocene, hexabromobenzene and hydroxymethylferrocene. The purification of 1,4,5,8-naphthalenetetracarboxylic acid and 1,4,5,8-naphthalenetetracarboxylic 1:8, 4:5-dianhydride, and the preparation of poly [(7-oxo-7*H*,10*H*-benz[*de*]imidazo-[4',5':5,6]benzimidazo[2,1-*a*]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL polymer) is also reported.

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I.

INTRODUCTION

The purpose of this research was to prepare various classes of compounds for use as intermediates in the synthesis of high temperature stable polymeric materials. The synthetic methods to be used are either improved established procedures or newly devised, unique procedures.

During this report period, work was conducted on the preparation of the following substances: (1) Benzidine 3,3'-dicarboxylic acid; (2) 6,6'-bis-([4H],3,1-benzoxazine-2,4-[1H]-dione); (3) diethyl 2,5-diaminoterephthalate; (4) pentafluorophenylphosphonous dibromide; (5) bis(pentafluorophenyl)-phosphinous bromide; (6) perfluoro-1-bromo-4-n-octylbenzene; (7) 1,1'-bis-(formyl)ferrocene; (8) poly[(7-oxo-7H,10H-benz[de]imidazo[4',5':5,6]-benz-imidazo-[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (referred to herein as BBL polymer); (9) 1,3-bis(phenylglyoxaloyl)benzene; (10) pyra-cyloquinone; (11) p,p'-oxydibenzil; and in securing and assaying lots of 1,1'-bis(hydroxymethyl)ferrocene, ruthenocene,and hexabromobenzene.

II.

RESULTS AND DISCUSSION

A. Benzidine 3,3'-Dicarboxylic Acid

The preparation of a considerable quantity of unpurified benzidine 3,3'-dicarboxylic acid was reported in AFML-TR-69-326 (Ref. 1). Also available was a quantity of commercial material comprising an aqueous slurry of benzidine 3,3'-dicarboxylic acid and its sodium salt. Elemental analyses indicated salt impurities in the benzidine 3,3'-dicarboxylic acid; therefore, in a portion of the work, the water-soluble impurities were washed out. Also an effort was made to precipitate from the commercial material the dihydrochloride salt, from which 3,3'-benzidine dicarboxylic acid could be recovered.

1. Purification of 3,3'-benzidine dicarboxylic acid: A total of 293 g. of unpurified benzidine 3,3'-dicarboxylic acid was ground, slurried under nitrogen with 9 liters of water overnight, and filtered off. After this operation was repeated two times, and the product was dried at 120°* (0.1 mm.) for 22 hr., 222 g. (76% recovery) of benzidine 3,3'-dicarboxylic acid was obtained. A sample of 114 g. of this product was forwarded to the Materials Laboratory.

2. Characterization: The infrared spectrum is reported in Figure 1.** The compound was also submitted for elemental analyses.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29. Found: C, 62.73; H, 4.52; N, 10.35; Cl, 1.17; ash, 1.92%.

3. Recovery of benzidine 3,3'-dicarboxylic acid from the commercial product: After 135 g. of the aqueous slurry of benzidine 3,3'-dicarboxylic acid and its sodium salt was mixed with 1 liter of 3N hydrochloric acid and heated to 58° and filtered, the filtrate was treated with 3.5 liters of concentrated hydrochloric acid. The precipitate, collected by filtration, washed with 100 ml. of 6N hydrochloric acid and dried 18 hr. at 120° (0.1 mm.) weighed 13.5 g. (10% recovery). The infrared spectrum (Figure 2) indicated that the product was chiefly benzidine 3,3'-dicarboxylic acid.

A similar experiment in which 381 g. of the slurry was treated with 1.95 liters of 2.8N hydrochloric acid and filtered, the soluble portion was mixed with 4 liters of concentrated hydrochloric acid. After the

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* All temperatures are reported in °C.

** All figures are found at the end of the report, p. 40.

precipitated material was filtered off, washed with 200 ml. of 6N hydrochloric acid, and dried 16 hr. at 100° (5 mm.), 47.2 g. of material (13% recovery) was obtained. The infrared spectrum (Figure 3) of this product indicated that it was chiefly the dihydrochloride.

4. Additional purifications via the hydrochloride: A 113-g. sample of unpurified benzidine 3,3'-dicarboxylic acid prepared in this laboratory was mixed with 650 ml. of 2.8N hydrochloric acid at 50° and filtered. After the filtrate was treated with 4.3 liters of concentrated hydrochloric acid and the precipitated material was filtered off, washed with 300 ml. of 6N hydrochloric acid, dried at 110° (1 mm.) for 33 hr., 59 g. (52% recovery) of material was obtained.

Anal. Calcd. for $C_{14}H_{14}N_2O_4Cl_2$ (the dihydrochloride): C, 48.71; H, 4.09; N, 8.12. Calcd. for $C_{14}H_{12}N_2O_4$ (the free base): C, 61.76; H, 4.44; N, 10.29. Found: C, 59.88, 59.49; H, 4.59, 4.57; N, 10.02, 9.91; ash, 1.27, 2.40.

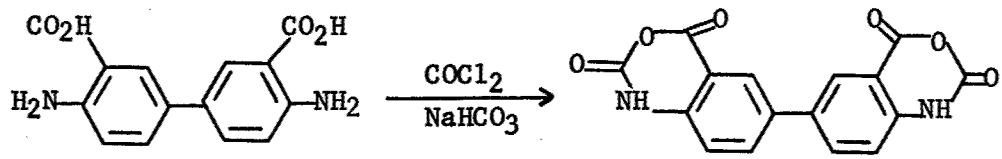
Although it had been intended to use the material purified in this way in the preparation of 6,6'-bis-([4H],3,1-benzoxazine-2,4-[1H]-dione), its purity warranted the additional purification necessary to submit it as a benzidine 3,3'-dicarboxylic acid sample to the Materials Laboratory. After it was mixed with 6 liters of water, filtered off, and dried for 22 hr. at 110° (1 mm.), a 39-g. sample was obtained, which was submitted for elemental analyses. Its infrared spectrum is reported in Figure 4.

Anal. Found: C, 62.17; H, 4.53; N, 10.18; Cl, 2.54; ash, trace.

A 6.2-g. sample was similarly obtained from 10 g. of the same impure benzidine 3,3'-dicarboxylic acid after it was dissolved in 60 ml. of 3.6N hydrochloric acid and reprecipitated with 200 ml. of aqueous sodium bicarbonate. This material was used in a small scale preparation of the "bisdione."

B. 6,6'-Bis-([4H],3,1-benzoxazine-2,4-[1H]-dione)

A small scale experiment was reported in AFML-TR-69-326 (Part I) in which satisfactory product was obtained in a low yield. After a larger scale experiment failed during this report period, several smaller scale experiments were attempted.



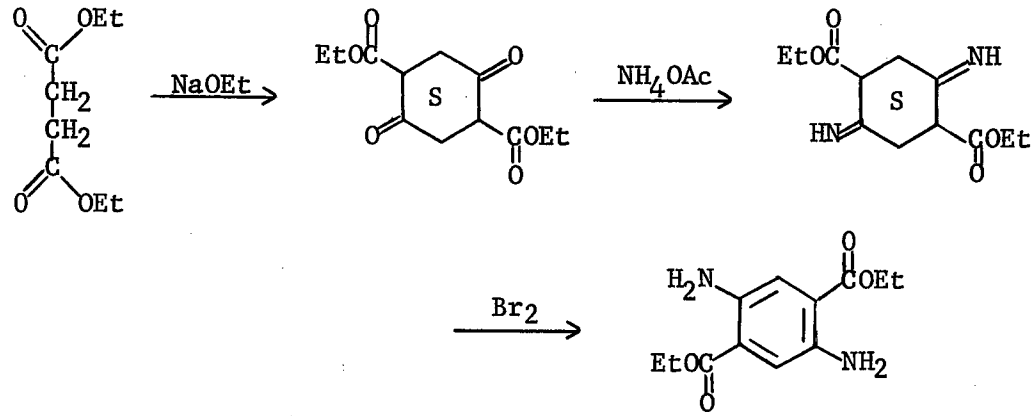
1. Large-scale experiment: After a mixture of 495 g. of sodium bicarbonate in 9 liters of water and 50 g. (0.184 mole) of benzidine 3,3'-dicarboxylic acid was warmed to 40° to effect solution, the stirred mixture was cooled to 10° and treated with gaseous phosgene for 5 hr. The precipitated material was filtered off, washed successively with 500-ml. portions of water, 10% acetic acid, methanol and petroleum ether (b.p. 60-90°), and dried at 105° (0.1 mm.) for 4 hr. The 37.8 g. of material, dissolved in 2 liters of boiling dimethylacetamide and filtered, did not precipitate when it was cooled to -30°. When the volume was reduced to 700 ml., no solids separated. Treatment of this solution with 5 liters of chilled methanol precipitated 18 g. of a gray black product and evaporation of the solution gave another 16 g. of material. The infrared spectra (Figure 5) of the two substances were similar and did not identify either as the "bisdione."

2. Small-scale experiments: After a mixture of 6 g. (0.022 mole) of benzidine 3,3'-dicarboxylic acid, 55 g. of sodium bicarbonate, and 1 liter of water was heated to 45° and filtered to remove 0.7 g. of insoluble material, the solution was treated with 1 g. of charcoal and refiltered. This filtrate was treated with phosgene at 10° for 4 hr., and then the insoluble product was filtered off and washed with 200-ml. portions of water, 10% acetic acid, methanol, and petroleum ether. When the filter residue was dried for 24 hr. at 100° (0.01 mm.), 3.3 g. of product was obtained. Its infrared spectrum is reported in Figure 6. When this material was heated at 150°, its infrared spectrum did not change. A portion of the material dissolved in dimethylacetamide solution and when treated with methanol gave a solid that liquefied on exposure to air.

Benzidine 3,3'-dicarboxylic acid hydrochloride (10 g., 0.029 mole), was dissolved in 800 ml. of distilled water containing 58 g. of sodium bicarbonate, and treated at 5° with phosgene, which was introduced through a fritted glass tube, for 4 hr. When the precipitated solids were collected, washed, and dried in the usual way, 5.8 g. of a product was obtained. Its infrared spectrum is reported in Figure 7. When the light green-colored material was heated at 135° (0.1 mm.) for 67 hr., the infrared spectrum did not change. When a 2-g. sample was dissolved in 50 ml. of dimethylacetamide and reprecipitated with 100 ml. of methanol, 0.4 g. was recovered which had an infrared spectrum similar to the other materials that had precipitated from dimethylacetamide. The infrared spectrum was not significantly changed when the product was mixed with a saturated sodium bicarbonate solution for 20 min.

C. Diethyl 2,5-Diaminoterephthalate

Pilot experiments for the synthesis of this compound were described in AFML-TR-69-326 (Ref. 1). In scale-up preparations, considerable difficulty had been encountered in the synthesis of the intermediate, diethyl 2,5-diaminoterephthalate. An alternate procedure was attempted for the final



step, the preparation of diethyl 2,5-diaminoterephthalate (Ref. 2). In this method, dehydrogenation was effected through the use of a palladium-on-charcoal catalyst. The conversion was not particularly good, and the best method was found to be a modification of the procedure provided by the project monitor in which bromine is used to bring about dehydrogenation. Improved yields were obtained with an excess of bromine above the stoichiometric amount owing to the loss of bromine through volatilization.

1. Synthesis: To 3.9 liters of absolute ethanol was added over a 5-hr. period 330 g. (14.4 g-atoms) of sodium. After the excess ethanol was distilled, the heavy white paste of sodium ethoxide was mixed with 7 liters of 1,4-dioxane and treated with 978 g. (5.6 moles) of diethyl succinate and stirred 17 hr. at room temperature. Subsequently, the mixture was heated at 50° for 4 hr., refluxed for 40 hr. The sodium salt, which was filtered off, was dispersed in 12 liters of ice water and treated with 40% acetic acid to a pH of 6. When the precipitated material was filtered off and recrystallized from ethanol, 426 g. (59%) of diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate, m.p. 126-128°,* was obtained (reported m.p. 126-127°) (Ref. 3). The infrared spectrum is reported in Figure 8.

Another preparation with 662 g. (3.8 moles) of diethylsuccinate afforded 63% of diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate, m.p. 128-129°.

* All melting points were determined using a Mel-Temp melting point apparatus.

After 4.42 (57.3 moles) of ammonium acetate was fused at 115°, 582 g. (2.28 moles) of diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate was added in 30 min. While water and other by-products were swept from the system with a stream of nitrogen, the mixture was heated to 130-135° and heating was continued at that temperature for 3 hr. After the hot mixture was poured into a stirred mixture of 15 liters of ice and water, the precipitated material was filtered off and washed with 60 liters of water and dried at 60° (11 mm.). An infrared spectrum (Figure 9) of the 518 g. of material, m.p. 117-132°, indicated that it was a mixture of diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate and diethyl 2,5-diimino-1,4-cyclohexanedicarboxylate. After the material was extracted twice with 95% ethanol, once with 6.7 liters and the second time with 5.4 liters, 255 g. of insoluble material, m.p. 126-128°, was identified as diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate. After the extracts were evaporated and the residue was recrystallized from 3 liters of 95% ethanol, 137 g. (24%) of diethyl 2,5-diimino-1,4-cyclohexanedicarboxylate, m.p. 167-172°, was obtained (reported, m.p. 177-180°) (Ref. 3). The infrared spectrum is reported in Figure 9.

a. Dehydrogenation with palladium charcoal in mesitylene: A mixture of 135 g. (0.53 mole) of diethyl 2,5-diimino-1,4-cyclohexanedicarboxylate, m.p. 167-172°, 13.3 g. of palladium on charcoal, and 1 liter of mesitylene was heated slowly to 144° and maintained at that temperature for 3 hr. During the heating period little foaming was observed. After the mixture was filtered hot, the combined filtrate and washings were chilled in an acetone-Dry Ice bath for 20 min. and the material that precipitated was filtered off and washed with 800 ml. of petroleum ether. After the residue was extracted with a mixture of 1.75 liters of ethanol and 700 ml. of water, 9.0 g., m.p. 120-165°, separated on cooling. An additional 54 g. was obtained when the solvent was evaporated. Evaporation of mesitylene filtrate and recrystallization of the residue from methanol gave 5.9 g., m.p. 138-150°. Recrystallization of the combined 54-g. and 5.9-g. fractions gave 37.4 g. (28%) of diethyl 2,5-diaminoterephthalate, m.p. 163-166°.

b. Dehydrogenation with bromine in sulfuric acid: A solution of 47 g. (0.29 mole) of bromine was added over a 30-min. period at 40° to a solution of 47 g. (0.19 mole) of diethyl 2,5-diimino-1,4-cyclohexanedicarboxylate, m.p. 120-165°, and the mixture was stirred at 50-55° for 3 hr. After nitrogen was passed through the mixture to purge the excess bromine, the mixture was poured into 2 liters of ice and water containing 26 g. (0.18 mole) of sodium sulfate. The sulfate salt, which was collected by filtration, was added to a solution of 500 g. of sodium acetate trihydrate in 1 liter of water to precipitate the free base, which was filtered off and washed with 400 ml. of water. When the filter residue was treated with charcoal and recrystallized twice from methanol and once from isopropyl alcohol, 7.6 g. (16%) of diethyl 2,5-diaminoterephthalate, m.p. 163-166°, was obtained.

A similar procedure with 47 g. (0.19 mole) of diethyl 2,5-diimino-1,4-cyclohexanedicarboxylate, one portion melting at 151-166° and the other at 121-149°, and 94 g. (0.60 mole) of bromine in 300 ml. of sulfuric acid gave 21 g. (45%) of diethyl 2,5-diaminoterephthalate.

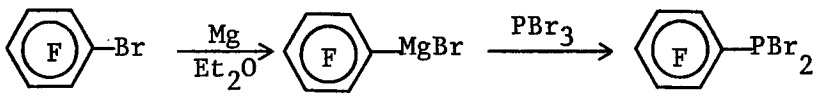
2. Physical properties: Diethyl 2,5-diaminoterephthalate was an orange-colored solid, m.p. 164-166°. Its infrared spectrum is reported in Figure 10.

3. Purity: An elemental analysis of the compound was obtained.

Anal. Calcd. for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.38; N, 11.10. Found: C, 57.36; H, 6.38; N, 10.47.

D. Pentafluorophenylphosphonous Dibromide

This material was prepared by the procedure described for pentafluorophenylphosphonous dichloride (Ref. 4).



1. Synthesis: The Grignard reagent of bromopentafluorobenzene, prepared by treating 3.0 g. (0.12 g-atom) of magnesium previously activated with a crystal of iodine with a solution of 24.7 g. (0.1 mole) of bromopentafluorobenzene in 50 ml. of dry ether, was refluxed 1.5 hr., cooled, transferred, and added dropwise to a rapidly stirred solution of 27.1 g. (0.10 mole) of phosphorus tribromide in 50 ml. of dry ether while the mixture was maintained at 10°. After a portion of the ether was evaporated, the mixture was filtered to remove a part of the magnesium salts. Fractional distillation of the filtrate gave 17.6 g. (49%) of pentafluorophenylphosphonous dibromide, b.p. 69-70° (0.9 mm.), [reported, 64-65° (1.1 mm.)] (Ref. 5).

Pentafluorophenyl Grignard reagent, prepared in 350 ml. of dry ether from 20.2 g. (0.83 g-atom) of magnesium, 172.9 g. (0.7 mole) of bromopentafluorobenzene, and a trace of iodine, was maintained at reflux temperature for 2 hr. before addition over a 1-hr. period to 189.7 g. (0.7 mole) of phosphorous tribromide in 350 ml. ether at 10°. Stirring was continued for 1 hr. After standing overnight, the ether was evaporated and the residue remaining was extracted at 50° with three 500-ml. portions of petroleum ether. By distillation through a 1 cm. x 15 cm., jacketed, unpacked Bantamware column, a 135.9 g. (54%) yield of perfluorophenylphosphonous dibromide was obtained.

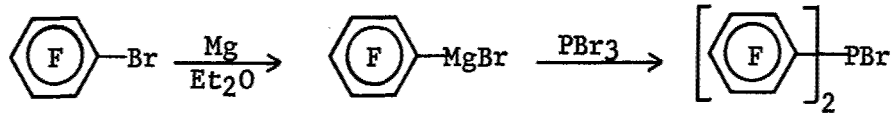
2. Physical properties: The substance boiled at 70-72° (1.2 mm.). The infrared spectrum is reported in Figure 11.

3. Purity: A GLC analysis at 105° on the SF-96 column showed only one peak.

Anal. Calcd. for $C_6F_5PBr_2$: C, 20.14; F, 26.54; Br, 44.66; P, 8.66. Found: C, 19.30; F, 24.31; Br, 45.10.

E. Bis(pentafluorophenyl)phosphinous Bromide

This material was prepared by the procedure described for bis(pentafluoropneny1)phosphinous chloride (Ref. 4).



1. Synthesis: The Grignard reagent of bromopentafluorobenzene, prepared by treating 6.0 g. (0.25 g-atom) of magnesium with 49.4 g. (0.2 mole) of bromopentafluorobenzene in 100 ml. of dry ether, was refluxed 1.25 hr., cooled, transferred, and added to a rapidly stirred solution of 27.1 g. (0.10 mole) of phosphorus tribromide while the mixture was maintained at 10°. After the ether was partly evaporated, the insoluble magnesium salts were filtered off and the filtrate fractionally distilled to obtain 16.1 g. (36%) of bis(pentafluorophenyl)phosphinous bromide, b.p. 112-115° (0.7 mm.). A forerun of 3.7 g. of pentafluorophenylphosphonous dibromide boiling at 73-96° (0.07 mm.) was also separated.

Pentafluorophenyl Grignard reagent, prepared in 800 ml. of ether from 395 g. (1.5 moles) of bromopentafluorobenzene, 48.0 g. (2.0 g-atoms) of magnesium, and a crystal of iodine, were maintained at reflux temperature for 2 hr. before addition to 216.8 g. (0.8 mole) of phosphorus tribromide in 400 ml. of ether at 10° ± 5° over a 1.75-hr. period. The temperature was raised to room temperature and stirring was continued 1 hr. The residue remaining after evaporation of the ether was extracted at 50° with three 500-ml. portions of petroleum ether. By fractional distillation through a Bantamware Vigreaux column, a 141-g. (40%) yield of bis(pentafluorophenyl)-phosphinous bromide, b.p. 102-104° (0.45 mm.), was obtained. The infrared spectrum is shown in Figure 12.

Anal. Calcd. for $C_{12}F_{10}PBr$: C, 32.39; F, 42.69; Br, 17.96; P, 6.97. Found: C, 31.83; F, 41.05; Br, 19.24.

2. Purity: GLC at 122° on a two-meter, 5%, SF-96 column failed to give a good analysis. A broad peak accounting for 7% of the total area preceded the main peak. This broad peak is believed to be a decomposition peak because its shape and size varied as the GLC conditions were changed.

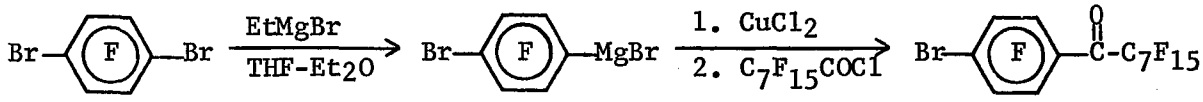
The sample was redistilled through a 1 cm. x 15 cm., jacketed, unpacked Bantamware column at 101-102° (0.02 mm.) in an effort to improve its elemental analysis.

Anal. Calcd. For $C_{12}F_{10}PBr$: C, 32.39; H, 0.0; F, 42.69; Br, 17.96; P, 6.97. Found: C, 31.51; H, 1.58; F, 40.86; Br, 18.90; P, 6.93.

The empirical formula calculated for this last analysis, $C_{12}H_7F_{10}PBr$, shows the correct ratio of atoms but the hydrogen content has not yet been explained. The infrared spectrum is shown in Figure 13.

F. Perfluoro-1-bromo-4-n-octylbenzene

A pilot run was initiated for the preparation of this substance by a method provided by the Materials Laboratory (Ref. 3).



1. Synthesis: A solution of 50 g. (0.16 mole) of 1,4-dibromotetrafluorobenzene in 417 ml. of tetrahydrofuran (previously dried over lithium tetrahydrido aluminate) was cooled to 0° and treated with 61 ml. (0.16 mole) of 2.6N (determined by titration) ethylmagnesium bromide in diethyl-ether. After the solution was stirred for 2.5 hr. at 0°, 21.8 g. (0.16 mole) of copper(II)chloride (dried to a constant weight) was added. Stirring was continued an additional 2 hr. at room temperature, and then the mixture was treated with 70 g. (0.16 mole) of perfluorooctanoyl chloride over a 30-min. period. The mixture was stored overnight, cooled in an ice-water bath, and treated with 450 ml. of 2.7N hydrochloric acid solution. After the mixture was filtered, 500 ml. of ether was added, the ether-tetrahydrofuran phase was separated, and the aqueous phase was extracted with three 50-ml. portions of ether. The combined ether-tetrahydrofuran phase and extracts were washed with 400 ml. of water, refiltered, dried 20 min. over magnesium sulfate, and the solvents were distilled off at atmospheric pressure. Fractional distillation in a 30-min. spinning-band column gave 28.8 g. of perfluorooctanoic acid, b.p. 55-60° (0.2-0.3 mm.) and 20.1 g. (20%) of 4-bromoperfluorooctanophenone, b.p. 95-96° (1.7 mm.) [reported 99° (2 mm.)] (Ref. 3). After several days' storage, the ketone solidified.

The procedure was scaled up with one change; copper(I)chloride was used in place of copper(II) chloride. To each of two flame-dried, 5-liter flasks was charged 154 g. (0.5 mole) of 1,4-dibromotetrafluorobenzene and approximately 1,270 ml. of $LiAlH_4$-treated tetrahydrofuran. Ethylmagnesium bromide (0.5 mole) in 190 ml. of dry ether was added at 0-2° to each flask over a 1-1/2-hr. period. Copper(I) chloride (49.5 g., 0.5 mole) was added in portions over a 30-min. period. Stirring was continued 5 hr. before adding 216 g. (0.5 mole) of perfluorooctanoyl chloride to each flask at 25-35° over a 1-1/2-hr. period. The reaction mixtures were stirred overnight before adding 600 ml. 6N HCl. The combined aqueous phase was extracted repeatedly with ether totaling 3.5 liters and the ether extract was washed three times with water. Solids which formed upon contact with water were removed by filtration before removal of the ether by distillation through a 31-cm. Vigreaux column at atmospheric pressure. Fractional distillation of the combined organic phase and extracted product gave a 465-g. (75% theory) yield of p-bromoperfluorooctanophenone, b.p. 96-98° (1.5 mm.). The infrared spectrum is shown in Figure 14.

A pilot test of the fluorination step was made with 13.3 g. (0.21 mole) of p-bromoperfluorooctanophenone, 8.4 g. (0.077 mole) of sulfur tetrafluoride and 6.2 g. (0.31 mole) of hydrogen fluoride in a rocking 95-ml. Monel reactor. The temperature was maintained at 180-183° for 12 hr. The yield of crude product was 11.6 g. (78%). A 7.2-g. (48%) purified yield of perfluoro-1-bromo-4-n-octylbenzene, m.p. 59-60°, [m.p. 53.1° (dsc) reported in the procedure supplied by LNP] was obtained by recrystallization of the crude product from 100 ml. of 95% ethanol.

Larger quantities of perfluoro-1-bromo-4-n-octylbenzene, m.p. 58-60°, were prepared in 72-74% theoretical yields in three autoclave runs of which the following is typical. A 1-liter, stainless steel, Autoclave Engineer Reactor containing 143 g. (0.23 mole) of p-bromoperfluorooctanophenone was purged at room temperature with sulfur tetrafluoride. The autoclave was cooled to assist in the transfer of 85 g. (4.3 moles) of hydrogen fluoride and 116 g. (1.1 moles) of sulfur tetrafluoride from sample bottles containing the desired quantities. The temperature of the stirred reactants was raised to 180° over a 4-hr. period and the temperature was maintained at 175-185° for 15 hr. The pressure reached 900 psig. After cooling to room temperature, the reactor was vented and the product was washed from the open reactor with four 250-ml. portions of ether. The etheral solution was washed with excess saturated sodium bicarbonate and then water until neutral. After magnesium sulfate drying, the ether was removed on a rotary evaporator. The crude product was dissolved in 1,200 ml. of refluxing 95% ethanol. After decanting from a small amount of yellow insoluble solid, the product was allowed to crystallize while stirring. The snow-white precipitate was separated on a Buchner funnel, pressed under a rubber dam and then dried 5 hr. in a vacuum oven at room temperature. The yield was 120 g. (72% theory) of perfluoro-1-bromo-4-n-octylbenzene.

2. Physical properties: The material melted at 58-59°. The infrared spectrum is shown in Figure 15.

G. Hexabromobenzene

A sample of 30 g. of hexabromobenzene was obtained from Aldrich Chemical Company for assay by GLC. Unsuccessful attempts were made to analyze this material on several polar and nonpolar type columns using a hydrogen flame detector. The material was satisfactorily characterized using a nonpolar column (6 ft. x 1/4 in. 20% SF 96 on Chromosorb P, 100 ml/min helium flow, thermal conductivity detector) by programming from 130-318°, see Figure 16. Considerable difficulty was experienced in obtaining a solvent in which hexabromobenzene was sufficiently soluble. Successful injection was achieved by using a hot chlorobenzene solution of the compound and a preheated syringe. The hexabromobenzene was found to be 93.2 ± 1% pure.

H. Ruthenocene

A 120-g. quantity of ruthenocene was obtained from Arapahoe Chemical Company, and subjected to GLC analysis. This material was found to be of very high purity, in excess of 99%, see Figure 17. The gas chromatographic conditions were: 107°, H_2 flame, 1 m. 10% PEG on Anakrom ABS, helium carrier - 17 psig.

I. Hydroxymethylferrocene (HMF)

A sample of 200 g. of hydroxymethylferrocene was obtained from Strem Chemical Company. GLC analysis of this material indicated that it was 93.1 ± 1% pure, see Figure 18, as compared to the 92.6 ± 1% purity of the standard hydroxymethylferrocene previously received from Strem, see Figure 19. The gas chromatographic conditions for this analysis were: 118°, H_2 flame, 1 m. 10% PEG on Anakrom ABS, helium carrier - 24 psig.

J. 1,1'-Bis(formyl)ferrocene

1. Study of physicochemical methods of characterization: The purity of 1,1'-bis(hydroxymethyl)ferrocene obtained from Strem Chemical Company (the only supplier) is reported to vary. Five ferrocene derivatives which were characterized during preliminary studies are:

1,1'-Bis(hydroxymethyl)ferrocene	(Strem)
Hydroxymethylferrocene	(Strem)
1,1'-Bis(methoxycarbonyl)ferrocene	(Strem)
1,1'-Bis(carboxy)ferrocene	(Strem)
1,1'-Bis(formyl)ferrocene	(LNP)

The physicochemical methods employed in these studies included TLC, GLC, NMR, IR, DTA, and elemental analysis. The pertinent data which were obtained as a result of this work, are set forth in Figures 20-31 and Table I. The main conclusions concerning the utility of the various physicochemical methods in the proposed preparation, are summarized as follows:

a. GLC appears to be the method of choice for following the progress of the oxidation of 1,1'-bis(hydroxymethyl)ferrocene to the dialdehyde (see Figure 26). The separation of the dialdehyde and its dihydroxy precursor on the SF-96 column is excellent and it is expected that any half oxidized product should also be separated.

b. GLC may be used to set specifications for 1,1'-bis(hydroxymethyl)ferrocene purity (see Figure 27). It appears that Strem's current stock of 1,1'-bis(hydroxymethyl)ferrocene is of good quality if this small sample is representative. Acceptance of large lots should be conditional on satisfactory TLC and GLC assay.

c. GLC can be used as a method to assay the purity of 1,1'-bis-(formyl)ferrocene (see Figure 28). In the sample supplied by LNP the retention time of the two minor impurities correspond to 1,1'-bis(hydroxymethyl)ferrocene and hydroxymethylferrocene. (Compare Figures 28 and 29.) The first might reasonably be expected but an equal quantity of unoxidized monohydroxymethyl derivative does not appear reasonable.

d. The reversal of the order of the retention times for the hydroxymethyl and the bis(hydroxymethyl) derivatives on the two types of GLC columns (compare Figures 29 and 30) may indicate intramolecular interaction of the hydroxyl groups, either hydrogen bonding or ether formation. Intramolecular interactions might assist in purification of these derivatives should methods of separation become necessary.

e. GLC analysis of Strem's 1,1'-bis(methoxycarbonyl)ferrocene (starting material for the preparation of 1,1'-bis(hydroxymethyl)ferrocene) indicates that it is 97.5% pure (see Figure 31).

f. Melting points (DTA) and elemental analyses are of limited value in determining the purity of these compounds. Samples were dried overnight in vacuo before elemental analyses. The broad melting range and poor elemental analyses on samples which are apparently reasonably pure by other standards do not recommend these time-honored methods for our criteria. Elemental analyses and DTA data are summarized in Table I.

TABLE I

ELEMENTAL ANALYSIS AND DTA ANALYSIS OF SUBSTITUTED FERROCENES

Elemental Analysis of Substituted Ferrocenes

Compound	Molecular Formula		C	H
1,1'-Bis (Hydroxymethyl)ferrocene	$C_{12}H_{14}O_2Fe$	Calcd:	58.57	5.73
		Found:	57.68	4.87
Hydroxymethylferrocene	$C_{11}H_{12}OFe$	Calcd:	61.15	5.60
		Found:	62.75	5.19
1,1'-Bis(methoxycarbonyl)ferrocene	$C_{14}H_{14}O_4Fe$	Calcd:	55.66	4.67
		Found:	55.48	4.59
1,1'-Bis(carboxy)ferrocene	$C_{12}H_{10}O_4Fe$	Calcd:	52.59	3.68
		Found:	50.21	3.48
1,1'-Bis(formyl)ferrocene	$C_{12}H_{10}O_2Fe$	Calcd:	59.54	4.16
		Found:	59.25	4.28

DTA Analysis of Substituted Ferrocenes

Compound	M.P. (°C, corr.)
1,1'-Bis(hydroxymethyl)ferrocene	88-101
Hydroxymethylferrocene	69-74
1,1'-Bis(methoxycarbonyl)ferrocene	104-110
1,1'-Bis(carboxy)ferrocene	228-253
1,1'-Bis(formyl)ferrocene	31-36

2. Batch analysis of 1,1'-bis(hydroxymethyl)ferrocene: Progress on this task was limited to the procurement of 1,1'-bis(hydroxymethyl)ferrocene (BHMF), 350 g. for LNP use and 350 g. for MRI conversion to the aldehyde. Five lots were received from the Strem Chemical Company and analyzed. Gas liquid chromatograms were determined using a Perkin Elmer Model 54 equipped with a hydrogen flame detector and using a 1 m. 10% PEG on Anakron ABS column. Operating temperature was 144° with a helium carrier gas flow of 18 psig. Samples were injected at attenuation X2 and at a retention time of 5 min. the main peak appeared (attenuation X4) followed by one minor peak at about 7.5 min. (X2) and a second substitutent at about 8.8-9.0 min. also at X2. In some samples the 7.5-min. peak was almost nonexistent while in other cases it was readily detected. All samples thus injected and attenuated were compared with the original standard (Lot 109B) (Figure 32). GLC and NMR data are summarized in Table II.

TABLE II

GAS LIQUID CHROMATOGRAMS OF SAMPLES OF 1,1'-BIS(HYDROXYMETHYL)FERROCENE (BHMF)

Lot No.	Sample Designation	Area Main Peak (%)	NMR Signal Ratio[a/]
109B	Original standard	97.1 ± 1	7.7
489B	Large batch	96.9 ± 1	8.9
491B	First crop	98.4 ± 1	8.1
491B	Second crop	96.8 ± 1	7.7
505B	Final batch	97.6 ± 1	6.3

a/ Ratio obtained from NMR spectra run in deuterated dimethylsulfoxide ($DMSO-d_6$) by dividing the integrated areas of aromatic and methylene protons by the integrated areas of alcoholic protons. The theoretical value for pure BHMF is 7.0.

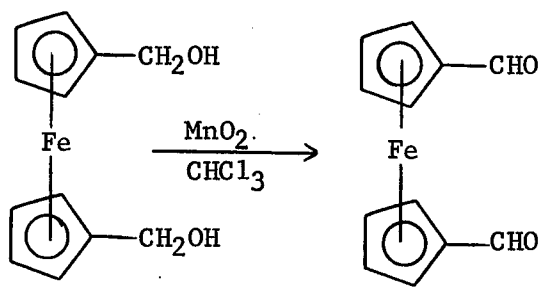
Lot 109B: A sample of this material was submitted to MRI by Strem before the 700-g. order (350 g. for LNP and 350 g. for MRI) was placed. The material was purified by Strem by washing the crude reaction product with cool diethyl ether. The material was characterized and deemed acceptable by LNP and MRI. On this basis, this material was designated as the "standard" sample and it was agreed that all other lots must analyze via GLC as good or better than it. A 125-g. sample of this material (which constituted the first part of LNP's 350-g. order) was shipped to MRI, characterized via GLC (see Figure 32) and NMR (see Figure 33), and forwarded to LNP on 19 May 1970.

Lot 489B: A sample of this material was submitted to MRI by Strem before shipment of the entire lot. This material according to Strem was purified in the same manner as Lot 109B, i.e., by washing the crude reaction product with cool diethyl ether. The material was analyzed via GLC (see Figure 34) and was deemed acceptable. However, replicated NMR analysis (see Figure 35) of the shipment revealed that the signal in the hydroxyl proton region could not be resolved into the characteristic triplet exhibited by Lot 109B and Lot 419B (first crop and second crop). A 225-g. sample of Lot 489B (which constitutes the final part of LNP's 350 g. order) was forwarded to LNP.

Lots 491B-1 and -2: Samples of these small lots were submitted to MRI by Strem before shipment of the entire lot. These lots were composed of two crystal crops (first and second crops) which according to Strem were obtained from an ether-washed reaction mixture by recrystallization from a benzene-petroleum ether solvent mixture. GLC analyses of the two crops (Figures 36 and 37) indicated that they were acceptable. The NMR spectra of the two crops (Figures 38 and 39) contained the characteristic hydroxyl triplet and were very similar to the spectrum of the standard sample.

Lot 505B: This lot was reportedly produced by the same procedure used for Lots 109B and 489B involving a cool diethyl ether washing of the crude reaction product. By GLC analysis (see Figure 40) the material is acceptable but as with Lot 489 the NMR analysis (Figure 41) fails to show "standard" quality.

3. Synthesis: 1,1'-Bis(formyl)ferrocene (BFF) was prepared by the oxidation of 1,1'-bis(hydroxymethyl)ferrocene using manganese dioxide as the oxidizing agent in a manner similar to the one described by Osgerby and Pauson (Ref. 6).



a. Pilot runs: Five pilot runs were carried out according to the procedure provided by the project monitor (Ref. 3). These runs are summarized in Table III. In all cases, GLC was used to follow the course of the reactions. The GLC data indicate that the reactions were readily initiated and proceeded rapidly towards completion upon the incremental addition of MnO_2 to the 1,1'-bis(hydroxymethyl)ferrocene (BHMF). Addition of the activated MnO_2 (Beacon Chemical Industries) required 20-25 min. By the time the reaction mixture was heated to reflux (total elapsed time 1 hr.), the reaction was nearly complete. After an additional 1 hr. refluxing, no BHMF remained, although in Runs Nos. 1, 2, and 3, the intermediate 1-formyl-1'-(hydroxymethyl)ferrocene (FHMF) could still be detected as a shoulder on the main product peak. Subsequent additions of 10 g. portions of fresh MnO_2 did not appear to drive the reaction any further to completion.

TABLE III

PREPARATION OF 1,1'-BIS(FORMYL)FERROCENE (PILOT RUNS)

Run No.	MRI Notebook No.	Moles BHMF	Strem Lot No. of BHMF	Yield (%)	Purity via GLC[a/]
1	70-93-48	0.03	505B	47.6	98.1
2	70-93-50	0.03	505B	54.0	97.6
3	70-93-59	0.03	505B	41.5	96.2
4	70-93-61A	0.03	491(1)	57.8	98.5
5	70-93-62B	0.03	491(1)	61.5	98.5

a/ All GLC data were obtained using a Perkin-Elmer Model 154 (H_2 flame, 178°, 2 m. 5% SF 96 on Gas Chrom Q, Helium carrier pressure - 15 psig, flow - 3.4, attenuation - X2).

A typical set of chromatograms (Figures 42 through 45) show the simultaneous disappearance of the starting material, BHMF; the formation and consumption of the intermediate product, FHMF; and the formation of the final product, BFF. A chromatogram of the reaction product after petroleum ether trituration and drying is shown in Figure 46, and a chromatogram of the product after recrystallization is shown in Figure 47. GLC analysis of a sample of BFF (purity = > 99%) received from LNP is shown in Figure 48.

An unknown impurity (retention time about 3.4 min.) in the reaction product was found not to be BHMF which has a retention time of about

2.9 min. The impurity was either a by-product of the reaction or a contaminant in the BHMF starting material. This impurity was not removed by the standard work-up procedure described in the LNP method (Ref. 3), but it was removed by recrystallizing the triturated product from cyclohexane; see Figure 47. It appears that slight differences in the size of the impurity peak are reflected in the small differences existing in the purity of BHMF samples received from Strem Chemical Company.

The yields of BFF (see Table III) ranged from 42-62%, and are considerably below the 80% range described in the LNP procedure (Ref. 3).

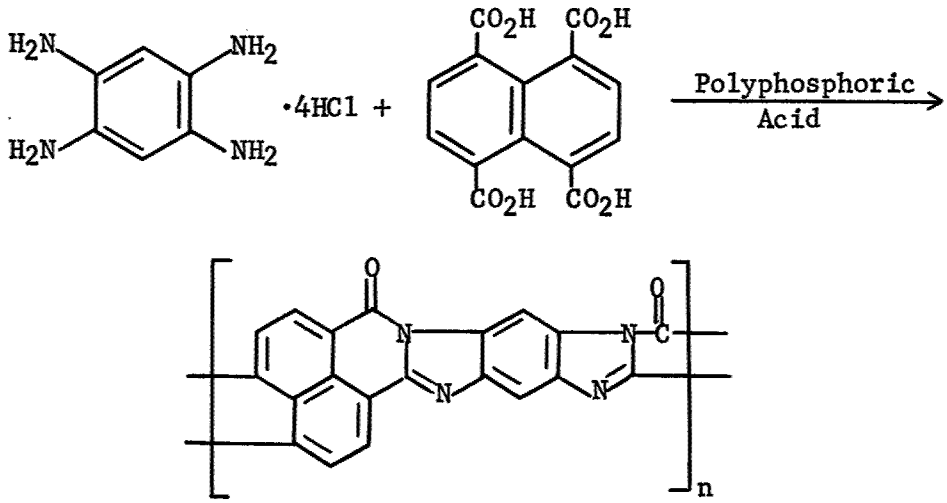
b. Production runs: 1,1'-Bis(hydroxymethyl)ferrocene, BHMF (310 g.), was divided into two equal portions and converted to BFF in two large production runs which were carried out simultaneously. The same procedure was employed as described for the pilot runs.

The two oxidations were conducted simultaneously in 12-liter flasks using MnO_2 (Beacon Chemical Industries) which has been activated according to a proprietary procedure (Ref. 3). To each flask containing a solution of BHMF in chloroform, was added MnO_2 in portions over a period of 1 hr. 50 min. The first small sample was removed for GLC analysis 1-1/2 hr. later, after the reaction mixtures had been heated and refluxed for 1/2 hr. At this point an additional charge of MnO_2 was added, which was equal to 20% of the original amount used, and refluxing continued for another 1/2 hr. The second small sample was removed for analysis. Another portion of MnO_2 (10% of original charge) was added and refluxing continued for one more hour, at which time the third and last sample was removed for GLC analysis. All three of the chromatograms in both runs were virtually identical, indicating the reaction had proceeded to completion after 1/2 hr. of refluxing. The work-up procedure gave 62% yields of product of 95.6% and 97.5% purity. This yield equaled the best yield obtained in the pilot runs, although it was still below the 80% range reported by LNP (Ref. 3). Chromatograms of the BFF products from the two runs are included as Figures 49 and 50.

All BFF products were combined and blended and a sample removed for GLC analysis. The 203.7 g. of BFF proved to be 98.0 ± 1% pure when analyzed by GLC as shown in Figure 51.

K. Poly[(7-oxo-7H,10H-benz[de]imidazo-[4',5':5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL Polymer)

Seven BBL polymer preparations were conducted according to a method supplied by the Materials Laboratory (Ref. 3) which is similar to a method described in the literature (Ref. 7).



The objective was to produce higher molecular weight polymer than produced in our laboratory previously (Ref. 1). The experimental work was guided by the assumption that reproducible production of the polymer could best be assured by careful purification of reactants. No problem was encountered in the purification of 1,2,4,5-tetraaminobenzene (TAB) but special attention was given to the purification of 1,4,5,8-naphthalene-tetracarboxylic acid (NTCA), which was found to be very difficult.

In addition, two BBL preparations were conducted according to a modified method using 1,4,5,8-naphthalenetetracarboxylic 1:8,4:5-dianhydride (NTDA) instead of NTCA. Although the NTDA samples which were employed, analyzed correctly, the condensations with TAB gave only low molecular weight BBL polymer.

1. 1,4,5,8-Naphthalenetetracarboxylic acid (NTCA):

a. Samples of "crude" NTCA: Three samples of "crude" NTCA were used as starting materials for the preparation of nine samples of "purified" NTCA.

NTCA No. 1: This sample was obtained from the Beaufort Chemical Company which is the only known commercial supplier of NTCA. American Amiline Products, GAF Company, American Hoechst Corporation, and the Aldrich Chemical Company no longer offer NTCA. The infrared spectrum of this sample as received (see Figure 52), corresponded closely to Sadtler's reference spectrum (20357) and had characteristic bands at 755, 1,085, and 1,165 cm^{-1}. Differential thermal analysis of the sample revealed no sharp transition below 300° but an infrared spectrum of the sample after heating to 300° (see Figure 53) corresponded closely to Sadtler's spectrum (25857) of 1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-dianhydride. Elemental analysis of the sample was in fair agreement with values for pure NTCA.

However, the low hydrogen and high carbon were indicative of the presence of some anhydride.

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.28; H, 2.65. Found: C, 55.89; H, 2.18.

NTCA No. 2 and NTCA No. 3: These samples were supplied by the Materials Laboratory which obtained the material under contract from the Celanese Corporation. One sample (NTCA No. 2) was received at MRI on 23 September 1969 and the other sample (NTCA No. 3) was received on 14 October 1970. NTCA No. 2 was used as the starting material for the preparation of the "purified" NTCA sample (NTCA No. 4) which was used to prepare a BBL polymer with an intrinsic viscosity of 2.95 (Ref. 1). NTCA No. 3 was used as a starting material for the preparation of two "purified" NTCA samples (NTCA Nos. 11 and 12) which were employed unsuccessfully in attempts to reproduce BBL polymer with high intrinsic viscosity. The infrared spectra of NTCA Nos. 2 and 3 were similar (compare Figures 54 and 55) but did not correspond to Sadtler's spectrum for NTCA. Although the two samples (NTCA Nos. 2 and 3) were supposed to be from identical lots, the elemental analyses of the two materials were significantly different.

Anal. Found: C, 53.77; H, 2.41; K, 0.86; Na, < 0.3 (NTCA No. 2). Found: C, 56.47; H, 2.69; K, 0.15; Na, 0.03 (NTCA No. 3).

b. Samples of "purified" NTCA: Nine samples of "purified" NTCA were prepared to determine the effect of various treatments and for use in the preparation of BBL polymer.

NTCA No. 4: A sample of NTCA No. 1 (Celanese crude) was reprecipitated twice by the following procedure: A 16.2-g. sample (0.053 mole) was dissolved by heating it for 15 min. at 60-70° in 75 ml. of an aqueous solution containing 13.8 g. (0.21 mole) of potassium hydroxide. After the pH was adjusted to 7 with dilute hydrochloric acid, the potassium salt of NTCA was precipitated with 250 ml. of cold methanol. The salt was redissolved in 200 ml. of cold water and reprecipitated with 50 ml. of 10% hydrochloric acid. After the acid was centrifuged off and washed three times with distilled water, it was dried overnight over sulfuric acid at 25° (0.1 mm.). The infrared spectrum (Figure 56) still showed a minor peak at 1770 cm^{-1}, which could be attributed to a minor portion of anhydride. The spectrum of the BBL polymer that was provided by the Materials Laboratory also shows a weak band in this region.

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.28; H, 2.65. Found: C, 53.23; H, 3.42; K, 0.10.

NTCA No. 5: This sample was prepared by subjecting a 250-g. sample of NTCA No. 1 ("crude" Beaufort) to three of the oxidation-decolorization treatments as described by Monsanto workers (Ref. 8) and recommended by the Materials Laboratory. The procedure was inoperable as given: 400 ml. (4.8 moles) of concentrated hydrochloric acid was insufficient to precipitate the NTCA from a solution of the acid containing 710 g. (10.7 moles) of 85% potassium hydroxide. Additional concentrated hydrochloric acid (400 ml.) was used to effect the precipitation. The recovery of NTCA was only 38% after three treatments, and a second 250 g. quantity of Beaufort crude was carried through the three steps.

Because the infrared spectrum showed more carbonyl absorption corresponding to anhydride than was present in the acid (NTCA No. 4) used previously, each batch was subjected to two additional treatments used previously (Ref. 1) involving precipitation of the potassium salt with methanol. The analyses of the batches gave nearly identical values. Therefore, the batches were combined and designated as NTCA No. 5. The anhydride peak was decreased by this treatment, but the infrared spectrum remained unchanged otherwise (Figure 57). The carbon-hydrogen analysis, DTA, and the infrared spectrum of this "purified" NTCA corresponded very closely to comparable data on the acid sample (NTCA No. 4), previously used to make high molecular weight BBL polymer (Figure 56), but all three analytical values indicated the product of this treatment to be something other than the pure acid. Additional work was conducted to characterize this "purified" NTCA and related NTCA samples. Results are detailed in the following paragraphs.

Elemental analyses, infrared spectra, conversion to anhydride, differential thermal analysis (DTA), neutralization equivalents, esterification, and paper chromatography data on this "purified" NTCA sample indicate that foreign molecules were trapped by the NTCA as it crystallized. The potassium in the NTCA may be bound as a salt of a carboxyl group or occluded potassium chloride.

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.28; H, 2.65. Calcd. for $(C_{14}H_8O_8)_{14}\cdot KCl$: C, 52.08; H, 2.50; K, 2.74. Calcd. for $C_{28}H_{15}KO_{16}$: C, 52.02; H, 2.34; K, 6.05. Found: C, 52.11; H, 2.86; K, 1.41, 1.61.

DTA: The NTCA No. 1 ("crude" Beaufort) showed no sharp transition up to 300°. The NTCA No. 5 ("purified" Beaufort) had a distinct transition at 161-165°, but dianhydride was produced as evidenced by the infrared spectra (Figures 53 and 58).

IR: Two forms of NTCA were differentiated by infrared spectra on a variety of samples. One form has characteristic bands at approximately 755, 1085, and 1165 cm^{-1}. This spectrum, referred to as Type I in the

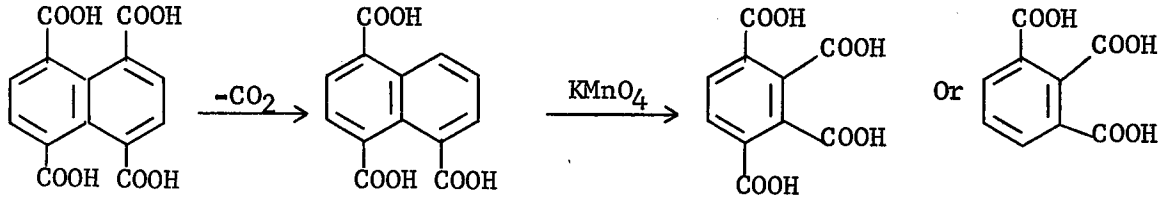
report, is the one reported by Sadtler for NTCA and was the one obtained on NTCA No. 1 ("crude" Beaufort) (Figure 52).

The second form of NTCA has an infrared spectrum (Type II) with characteristic bands at 775, 815-82 and 875 cm^{-1}. This form is produced by acidification of aqueous solutions of the sodium or potassium salt of NTCA as described by Monsanto workers (Ref. 8). The NTCA No. 1 ("crude" Celanese) supplied this laboratory by LNP in September 1969 is predominantly Type II (Figure 54).

After subjecting NTCA No. 1 to the first series of three oxidation-decolorization treatments which concluded with a precipitation by acidification of the sodium salt, the spectrum had changed from Type I to Type II (Figure 59). The additional steps in the preparation of NTCA No. 5 resulted in no appreciable change (Figure 57), even though the additional steps terminated with acidification of the potassium salt, not the sodium salt.

NE: Neutralization equivalents of several acid samples were determined in 50:50 DMF-water. Titration of 0.2-g. samples of NTCA No. 5 ("purified" Beaufort) with 0.1N methanolic potassium hydroxide to the inflection point of a potentiometric plot gave neutralization equivalents of 90.2, 91.7, and 93.8 for triplicate determinations. The calculated neutralization equivalent for $C_{28}H_{15}KO_{16}$, assuming a potassium salt of one of the eight -COOH groups is 92.3 and for $(C_{14}H_8O_8)_4 \cdot KCl$ is 80.7. (Neutralization equivalents can be misleading if the presence of neutralized carboxyl groups is not recognized. Dissolution of an alkali metal carboxylate in the PPA polymerization medium gives a -COOH group not detected by a neutralization equivalent determination.

TLC: R_f values have been reported for NTCA and a number of polycarboxylic acids (Ref. 9). Benzene polycarboxylic acids appeared to be reasonable products of the permanganate oxidation and we sought to identify them through TLC using a solvent of ethyl acetate-glacial acetic acid-water (2:1:1 v/v) containing bromophenol blue (0.015% w/v) and sodium acetate (0.05% w/v) as the incorporated indicator.



R_f 99-100 53-63 67-76

An impurity shown to be present in NTCA No. 5 ("purified" Beaufort) had an R_f between 0.69-0.77, which corresponds to 1,2,3-benzene-tricarboxylic acid. The amount appeared to be small.

GLC: The tetramethylester of NTCA No. 5 was prepared with diazomethane generated from nitrosomethylurea in DMF-ether as solvent. GLC shows one major component (90% minimum) (Figure 60).

Conclusions: The composition of the precipitated NTCA obtained by acidification of aqueous solutions of the alkali metal salts of NTCA apparently depends upon the conditions employed. Although the NTCA purification procedure has been used successfully a number of times to obtain quality acid (Refs. 10-13), in our hands we did not get free acid. Since NTCA No. 2 supplied by the Materials Laboratory appeared to be a mixture of Type I and Type II as indicated by the infrared spectrum (Figure 54) it is suspected that the composition of NTCA samples purified by the Monsanto method may have varied considerably in other laboratories.

NTCA Nos. 6, 7, and 8: These samples were prepared by contacting samples of NTCA No. 5 ("purified" Beaufort) with various dosages of concentrated hydrochloric acid for various lengths of time: NTCA No. 6, 1 g. with 100 ml. 12N HCl for 15 min. (see Figure 61); NTCA No. 7, 5 g. with 165 ml. 6N HCl for 20 hr. (see Figure 62); and NTCA No. 8, 5 g. with 600 ml. 6N HCl for 66 hr. (See Figure 63). Figure 61 shows that approximately 15 min. slurrying with concentrated hydrochloric acid liberated a little of the Type I material and Figure 62 shows that overnight stirring with 6N hydrochloric acid resulted in Type I spectrum comparable to the Beaufort starting material.

Anal. Calcd. for $C_{14}H_8O_8$ (free acid): C, 55.28; H, 2.65. Found for NTCA No. 7: C, 53.69; H, 2.24. Found for NTCA No. 8: C, 58.10; H, 2.08. Calcd. for $C_{14}H_4O_6$ (dianhydride): C, 62.70; H, 1.50.

The trend that the hydrogen content decreases as carbon increases suggests that water is being lost. Although the elemental analysis shown above suggests anhydride formation, the infrared spectrum (Figure 63) is not that expected of NTCA having appreciable quantities of the anhydride produced by heating NTCA to 300° (Figure 53). It is possible that intermolecular and intramolecular anhydrides are complicating the interpretation. The anhydride produced thermally may not be the same type as that produced in acid solution. If the two types of NTCA are due to two crystal structures, the geometric relationship of carboxyl groups in one may favor anhydride formation more than the other. Nevertheless, the best polymer to date has been obtained from Type II NTCA produced by avoidance of lengthy contact with excess hydrochloric acid.

When acid treated NTCA (Nos. 7 and 8) failed to give good polymer, two additional samples of NTCA were prepared with special attention being given to the rate at which the NTCA was precipitated and to careful washing of the salt. Treatment of one sample was that described in the Monsanto reference (Ref. 8). The other sample was carried through the isolation of the potassium salt (Ref. 1).

NTCA No. 9: A sample of NTCA No. 5 (20.0 g., 0.066 mole) was dissolved in a solution of aqueous base consisting of 19.8 g. (0.30 mole) of 85% pelleted KOH in 265 ml. water. Charcoal, 3.0 g., in 90 ml. of methanol was added and the stirred slurry brought to a boil and filtered hot. The filtrate was again decolorized hot with another 3.0 g. portion of activated charcoal and filtered through a thin pad of Celite. The filtrate was then rapidly stirred as 12N HCl was slowly added. A pH of 0.85 was reached after a slight excess of acid had been added. The finely divided acid was filtered and reslurried with 355 ml. of a 1:3 mixture of methanol and water. The solids were washed with 100 ml. of methanol and then resuspended in 250 ml. of water in a 500 ml. Erlenmeyer flask. The slurry was subjected to a 5 min. sonic mixing in an ultrasonic bath by slowly raising and lowering the flask. The solids were treated as before, that is, again slurried with a 1:3 mixture of methanol-water and finally with methanol before vacuum desiccation over P_2O_5. After the 19 hr. drying period, 17.0 g. (85% recovery) of NTCA remained (NTCA No. 9). The infrared spectrum was Type II (Figure 64).

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.28; H, 2.65. Found: C, 54.19; H, 2.89; K, 0.11.

One-half of this material was used in polymerization 70-4 and the remainder treated as described in the next paragraph.

NTCA No. 10: A sample of NTCA No. 9 (8.5 g., 0.028 mole) was dissolved in aqueous base consisting of 85% KOH (7.7 g., 0.117 mole) in 40 ml. distilled water. The NTCA was added with stirring and heated to 80°. The clear solution was cooled to 5° and 6N HCl was added slowly and carefully until hydrion paper indicated a pH of about 7.0. At this stage, 1 g. decolorizing carbon was added and the mixture was filtered through a thin pad of Celite. The potassium salt was precipitated from the cold filtrate by addition of 450 ml. of methanol and overnight refrigeration. The potassium salt was removed by filtration and dissolved in 112 ml. water. This aqueous solution (pH 8.4) was stirred briskly while titrating slowly with 12N HCl. Excess acid (0.12 equivalent) was added. The precipitated acid was treated exactly as described in the preceding paragraph, that is, it was subjected to methanol mixing, then redissolved in water, mixed ultrasonically and again methanol treated and dried for 16 hr. over P_2O_5 at 0.1 mm. This material amounted to 6.0 g. (71% recovery) (NTCA No. 10). The infrared spectrum was Type II (Figure 65).

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.28; H, 2.65. Found: C, 54.22; H, 2.86; K, 0.08.

NTCA No. 11: A sample of NTCA No. 3 (16.2 g., 0.053 mole) was dissolved in a warm solution of aqueous base consisting of 13.8 g. (0.21 mole) of 85% KOH in 75 ml. of water. The solution was cooled to 50° and adjusted to pH 7 with 6N HCl. The solution was filtered to remove trace amounts of undissolved impurities, then concentrated to approximately two-thirds of its original volume. This solution was cooled and the potassium salt precipitated by addition of 250 ml. of methanol. The salt was filtered and dissolved in 200 ml. of distilled water. The free acid was precipitated by addition of 50 ml. of 10% HCl, filtered, and redissolved in a basic solution of 13.8 g. (0.21 mole) of 85% KOH in 75 ml. of water. The purification procedure described above was repeated an additional two times. After the final precipitation of the free acid, it was filtered and washed three times by slurry with 250 ml. of water. The solid was vacuum dessicated over P_2O_5 for 20 hr. The material amounted to 11.9 g. (73.5% recovery). Infrared spectrum was Type II (Figure 66).

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.28; H, 2.65. Found: C, 51.88; H, 2.64; K, 2.99; Na, 0.034.

NTCA No. 12: A sample of NTCA No. 3 (10.0 g., 0.033 mole) was dissolved in 132 ml. of 1.0N KOH which was warmed to 60°. The solution was cooled to room temperature and adjusted to pH 7 (pH meter) with 2.80 ml. of 1N HCl. This solution was stirred with 1.0 g. of decolorizing charcoal and filtered through Celite. The filtrate was concentrated on a rotary evaporator while keeping the solution temperature at 40°. To the concentrate (cooled to 5°) was added 250 ml. of anhydrous methanol. The milky mixture was stirred for 20 min. and filtered. The precipitated potassium salt was dissolved in water and the aqueous solution filtered to remove traces of insoluble material. Rapid addition of 139 ml. of 1N HCl precipitated the free acid which was quickly filtered and redissolved in 132 ml. of 1.0N KOH. After the purification procedure was repeated, the precipitated acid was washed three times by slurry with 100 ml. of water and one time with anhydrous methanol. After vacuum drying over P_2O_5, 7.2 g. (72% recovery) of NTCA remained. Infrared spectrum was Type II (Figure 67).

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.28; H, 2.65. Found: C, 54.56; H, 2.71; K, 0.03.

The physicochemical properties of all NTCA samples are summarized in Table IV.

TABLE IV

CHARACTERIZATION OF SAMPLES OF 1,4,5,8-NAPHTHALENETETRACARBOXYLIC ACID (NTCA)

NTCA No.	Description of NTCA Sample	Elemental Analysis % C	% H	% K	% Na	DTA (°C)	IR Spectrum	BBL Polymer $[\eta]$[a]	No.
1	"Crude" NTCA (Beaufort)	55.89	2.18	--	--	[b]	Figure 52	--	--
2	"Crude" NTCA (Celanese)[c]	53.77	2.41	0.86	< 0.3	--	Figure 54	--	--
3	"Crude" NTCA (Celanese)[d]	56.47	2.69	0.15	0.03	138-165	Figure 55	--	--
4	"Purified" NTCA No. 2	53.23	3.42	0.10	--	--	Figure 56	2.95	69-1
5	"Purified" NTCA No. 1	52.01	2.86	1.51	< 0.3	161-165	Figure 57	1.57	70-1
6	"Treated" NTCA No. 5	--	--	--	--	--	Figure 61	--	--
7	"Treated" NTCA No. 5	53.69	2.24	0.029	< 0.3	--	Figure 62	0.69	70-2
8	"Treated" NTCA No. 5	58.10[e]	2.08	--	--	--	Figure 63	0.67	70-3
9	"Purified" NTCA No. 5	54.19	2.89	0.11	--	--	Figure 64	0.66	70-4
10	"Purified" NTCA No.9	54.22	2.86	0.08	--	--	Figure 65	1.41	70-5
11	"Purified" NTCA No. 3	51.88	2.64	2.99	0.034	147-149	Figure 66	1.55	70-6
12	"Purified" NTCA No. 3	54.56	2.71	0.03	--	151-177	Figure 67	1.11	70-7

a/ See Table V for experimental viscosimetric data.
b/ No sharp transition up to 300°.
c/ Received from the Materials Laboratory on 9/23/69.
d/ Received from the Materials Laboratory on 10/14/70.
e/ Average of duplicate determinations.

2. 1,4,5,8-Naphthalenetetracarboxylic 1:8,4:5-dianhydride (NTDA): The preparation and/or purification of NTDA was investigated after repeated efforts to obtain consistently pure NTCA had failed.

a. Commercial sources of NTDA: The dianhydride was available from three commercial sources: Aldrich Chemical Company, Chemical Procurement Labs, Inc., and K&K Laboratories, Inc. A small sample was obtained from each supplier and analyzed. None of the NTDA samples obtained from the commercial sources analyzed correctly.

Anal. Calcd. for $C_{14}H_4O_6$: C, 62.70; H, 1.50. Found: (Aldrich) C, 60.15; H, 1.90, IR Figure 68; (Chemical Procurement) C, 60.52; H, 1.59, IR Figure 69; (K and K Laboratories) C, 56.10; H, 2.35, IR Figure 70.

Gallard Schlisinger was also listed as a supplier but was out of stock and would quote only kilogram quantities.

b. Attempted preparation of NTDA from NTCA via refluxing with acetic anhydride: A 1-g. sample of Celanese NTCA was refluxed for several hours with 200 ml. of acetic anhydride. The anhydride solution became very dark; however, solution of NTCA was never accomplished. The dark gray acid was filtered off and dried in vacuo. After drying, the infrared spectrum of the product was identical to Aldrich NTDA. Attempted sublimation of the crude NTDA at 300° and 0.02 mm. Hg was unsuccessful.

c. Preparation of NTDA from NTCA via refluxing in glacial acetic acid: To 0.5 g. of Celanese NTCA was added glacial acetic acid until solution resulted. For complete solution, 500 ml. of the acid was required at reflux temperature. On cooling to room temperature, a solid separated out and was filtered off. The product was dried in a vacuum desiccator to obtain 0.36 g. (81% yield) of a light fluffy yellow powder which analyzed correctly as NTDA. An infrared spectrum (Figure 71) was identical to the Aldrich material. (This material was designated NTDA No. 1 and was used in BBL polymerization No. 71-1.)

Anal. Calcd. for $C_{14}H_4O_6$: C, 62.70; H, 1.50. Found: C, 62.89; H, 1.47.

d. Attempted purification of NTDA via chemical dehydration and sublimation (Ref. 14): To 10 g. of the crude NTDA from Aldrich was added 200 ml. of acetic anhydride and the mixture was heated at reflux for 1 hr. The solid was filtered off, dried, and placed in a small sublimator. A small amount of yellow sublimate was obtained but it was small compared to the total product. The majority of the material did not sublime but appeared to shrink and decompose. The oil bath temperature reached a maximum of 330°C at 0.025 mm. Hg pressure on the system during the attempted sublimation.

e. Purification of NTDA via recrystallization from nitrobenzene (Ref. 15): To 10 g. of NTDA from Aldrich was added nitrobenzene until solution was completed. Complete dissolution required approximately 500 ml. of solvent at 200°. The solution was filtered with difficulty because of a fine dark solid impurity that clogged the filter paper. On cooling, a crystalline mass (pale yellow needles) separated. The crystalline product was collected and dried at 80° under high vacuum for 4 hr.

Anal. Calcd. for $C_{14}H_4O_6$: C, 62.70; H, 1.50. Found: C, 63.66; H, 1.95.

The NTDA was recrystallized a second time from nitrobenzene. The product after drying in vacuo was analyzed again. Found: C, 64.89; H, 1.63. This material was then dried at 100°/0.1 mm. Hg for 18 hr. and reanalyzed. Found: C, 63.35; H, 1.53. This material because of the high boiling point of the recrystallizing solvent (209°) was again dried at 180° for 3 hr. at 0.05 mm. Hg. At this temperature and pressure, some sublimation did occur. Found: C, 63.03; H, 1.42.

f. Purification of NTDA via recrystallization from glacial acetic acid: To 4 g. of the NTDA from Aldrich was added 4 liters of glacial acetic acid and the mixture heated with stirring to reflux. The clear solution obtained at reflux was filtered hot and a solid precipitated from the filtrate on cooling. The solid, a fine yellow powder, was dried in a vacuum oven at 80° and 0.05 mm. Hg and analyzed. (This material was designated NTDA No. 1 and was used in BBL polymerization No. 71-2.)

Anal. Calcd. for $C_{14}H_4O_6$: C, 62.70; H, 1.50. Found: C, 62.94; H, 1.25.

3. 1,2,4,5-Tetraaminobenzene tetrahydrochloride (TAB): Two 120-g. portions of TAB purchased from Burdick and Jackson Laboratories were purified following the procedure used previously (Ref. 1) and initially supplied by the project monitor (Ref. 3). Charcoal treatment in deoxygenated water gave virtually colorless filtrates which were combined. The recovery was 56% (139.3 g.) after drying to constant weight over P_2O_5 at 80° and 0.1 mm. in a vacuum oven. The characteristic color change from pink to blue-violet was observed. Elemental analyses on material as received and after purification are reported.

Anal. Calcd. for $C_6H_{14}N_4Cl_4$: C, 25.37; H, 4.97; N, 19.73; Cl, 49.93. Found: (before and after) C, 25.66, 25.57; H, 4.76, 5.08; N, 19.90, 19.70; Cl, 49.71, 49.52.

The desiccated TAB gradually turned gray upon standing. Therefore, it was repurified before polymerization and stored under different conditions.

TAB (121.7 g., 0.43 mole) was dissolved in deoxygenated distilled water, charcoal treated, filtered, and the salt reprecipitated with concentrated hydrochloric acid as previously reported. The washed solids were retained in a covered desiccator over Drierite and small amounts dried at 80° (0.1 mm.) over P_2O_5 as needed for each subsequent polymerization run.

4. Polymerization: Seven small-scale polymerizations (70-1 through 70-7) were made using NTCA and two small-scale polymerizations (71-1 and 71-2) were made using NTDA. In each run with NTCA the stoichiometry has been figured on the molecular weight of pure NTCA, 304.21, even though analyses did not indicate pure acid. No attempt was made to adjust the stoichiometry to an effective NTCA content. The procedure was that used previously (Ref. 1) and initially provided by the project monitor (Ref. 3). All runs were 0.01 molar scale. The viscosimetric data for each polymer preparation is summarized in Table V.

5. Conclusions: The low intrinsic viscosities call for a new approach. In a private communication it was established that Monsanto workers obtained their best results with NTCA having a low carbon analysis. The present study confirms this trend. The NTCA which precipitates upon acidification of an aqueous solution of the salt of NTCA invariably has a low carbon analysis and is characterized by a Type II spectrum. Lengthy precipitation or contacting with excess mineral acid results in NTCA with a higher carbon content. With slow precipitation and extensive washing the carbon analysis approaches theoretical (ca. 1% low) but the spectrum remains Type II. Contact with excess aqueous hydrochloric acid not only raises the carbon content but results in Type I spectra. The treatment with excess hydrochloric acid over a long period of time at room temperature results in a product which has higher than theoretical carbon content.

The secondary approach to BBL polymer via NTDA, also gave low intrinsic viscosities even after purification of the dianhydride reactant.

L. 1,3-Bis(phenylglyoxaloyl)benzene

This compound was synthesized according to the procedure of Wrasidlo and Augl (Ref. 16).

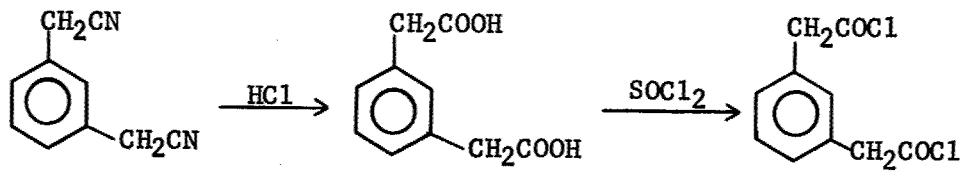


TABLE V

VISCOSIMETRIC DATA ON BBL POLYMERS

BBL Polymer 69-1 (Prepared using NTCA No. 4)

Times (sec.)	Conc. C (g/dl)	Avg. T. (sec.)	η_r	η_{sp}	$\frac{\eta_{sp}}{C}$	$\frac{\ln \eta_r}{C}$
196.8, 196.2, 196.8	0.5	196.6	3.2821	2.282	4.56	2.38
113.2, 113.1	0.25	113.1	1.8881	0.888	3.55	2.53
85.5, 85.6	0.125	85.5	1.4274	0.427	3.42	2.85
59.9, 59.9, 60.0	Solvent[a]	59.9			$[\eta] = 2.95$[b]	

BBL Polymer 70-1 (Prepared using NTCA No. 5)

119.4, 119.3, 119.4	0.5	119.4	2.0551	1.055	2.11	1.24
84.1, 84.0, 84.0	0.25	84.0	1.4458	0.446	1.78	1.47
70.1, 70.2, 70.3	0.125	70.2	1.2083	0.208	1.66	1.46
58.2, 58.1, 58.1	Solvent[a]	58.1			$[\eta] = 1.57$[b]	

BBL Polymer 70-2 (Prepared using NTCA No. 7)

83.1,82.9, 83.3	0.5	83.1	1.4205	0.421	0.84	0.72
69.9, 69.8, 69.7	0.25	69.8	1.1932	0.193	0.77	0.71
63.7, 63.9, 63.8	0.125	63.8	1.0906	0.091	0.73	0.69
58.5, 58.4, 58.5	Solvent[a]	58.5			$[\eta] = 0.69$[b]	

BBL Polymer 70-3 (Prepared using NTCA No. 8)

94.4, 94.4, 94.3	0.5	94.4	1.558	0.558	1.116	0.89
73.5, 73.5, 73.4	0.25	73.5	1.213	0.213	0.852	0.77
66.6, 66.6, 66.7	0.125	66.63	1.100	0.100	0.800	0.76
60.6, 60.7, 60.5	Solvent[a]				$[\eta] = 0.67$[b]	

BBL Polymer 70-4 (Prepared using NTCA No. 9)

91.4, 91.5, 91.5	0.5	91.5	1.510	0.510	1.02	0.82
73.0, 72.9, 72.9	0.25	72.9	1.203	0.203	0.812	0.74
66.6, 66.6, 66.5	0.125	66.57	1.099	0.099	0.792	0.75
60.6, 60.7, 60.5	Solvent[a]				$[\eta] = 0.66$[b]	

BBL Polymer 70-5 (Prepared using NTCA No. 10)

119.2, 119.3, 119.1	0.5	119.2	1.967	0.967	1.93	1.35
84.1, 84.2, 84.4	0.25	84.2	1.389	0.389	1.556	1.32
72.4, 72.4, 72.4	0.125	72.4	1.195	0.195	1.558	1.425
60.6, 60.7, 60.5	Solvent[a]				$[\eta] = 1.41$[b]	

TABLE V (concluded)

BBL Polymer 70-6 (Prepared using NTCA No. 11)

Times (sec.)	Conc.C (g/dl)	Avg. T (sec.)	η_r	η_{sp}	$\frac{\eta_{sp}}{C}$	$\frac{\ln \eta_r}{C}$
122.2, 122.4, 122.5	0.5	122.4	2.1031	1.103	2.26	1.49
85.4, 15.2, 85.2	0.25	85.3	1.4656	0.466	1.86	1.53
70.4, 70.3, 70.5	0.125	70.4	1.2096	0.210	1.68	1.52
58.2, 58.2, 58.1	Solvent[a]	58.2			$[\eta] = 1.55$[b]	

BBL Polymer 70-7 (Prepared using NTCA No. 12)

104.1, 104.5	0.5	104.35	1.670	0.670	1.34	1.03
104.4, 104.5						
81.1, 81.3	0.25	81.12	1.2985	0.2985	1.19	1.05
81.0, 81.1						
71.5, 71.6	0.125	71.56	1.146	0.146	1.17	1.09
71.6	Solvent[a]	62.47			$[\eta] = 1.10$[b]	

BBL Polymer 71-1 (Prepared using NTDA No. 1)

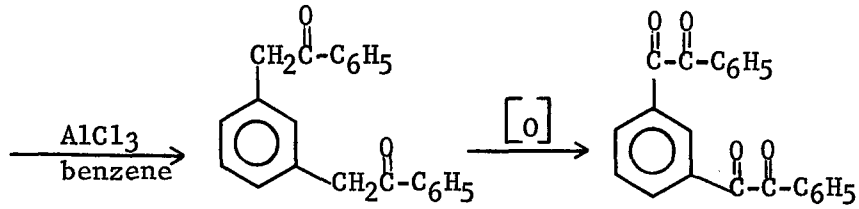
71.5, 71.5, 71.5	0.5	71.5	1.144	0.144	0.288	0.262
66.5, 66.4, 66.4	0.25	66.4	1.062	0.062	0.248	0.232
64.4, 64.4, 64.5	0.125	64.4	1.031	0.031	0.248	0.240
62.5, 62.4, 62.5	Solvent[a]	62.5			$[\eta] = 0.270$[b]	

BBL Polymer 71-2 (Prepared using NTDA No. 2)

75.4, 75.4, 75.4	0.5	75.4	1.205	0.205	0.410	0.380
68.9, 68.9, 68.8	0.25	68.9	1.101	0.101	0.404	0.381
65.3, 65.3, 65.5	0.125	65.4	1.046	0.046	0.368	0.314
62.6, 62.5, 62.4	Solvent[a]	62.5			$[\eta] = 0.380$[b]	

[a] Methanesulfonic acid.

[b] Intrinsic viscosities were obtained in the conventional manner from the extrapolated intercepts o the plots of the reduced specific viscosities and the inherent viscosities.



It was found that careful temperature control was necessary in the conversion of m-phenylenediacetic acid to the acid chloride. In pilot scale experiments using an ordinary mantle to maintain the reaction at reflux temperatures, the only material isolated was an intractable solid. An oil bath held at 80-85° allowed the reaction to proceed smoothly to the desired product.

The Friedel-Crafts acylation of the acid chloride to 1,3-bis(phenylacetyl)benzene also presented problems. The use of commercial anhydrous aluminum chloride resulted in a heavy oil which could not be crystallized. By employing a modified aluminum chloride catalyst (Ref. 17) (prepared via equilibration of a 1:10 weight ratio of $AlCl_3 \cdot 6H_2O$ and $AlCl_3$) the desired condensation was obtained. The last step to 1,3-bis(phenylglyoxaloyl)-benzene went smoothly in 49% yields.

1. Synthesis: m-Phenylenediacetonitrile (200 g., 1.28 mole) was refluxed for 48 hr. with 2 liters of 6N hydrochloric acid. The solution was cooled to room temperature and the white precipitate was filtered and washed with cold water. The solid was dissolved in a concentrated potassium hydroxide solution which was then decolorized with activated charcoal and filtered. The filtrate was cooled to ice-bath temperatures and the pH adjusted to approximately 2 with concentrated hydrochloric acid. The precipitated acid was filtered and washed thoroughly with cold water. After vacuum drying at 50° the yield of product was 213 g. (85%), m.p. 178-180° (reported m.p. 174-175°). The infrared spectrum is shown in Figure 72.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.09; H, 5.44.

Two additional runs by the same procedure gave 438 g. of m-phenylenediacetic acid with an average yield of 81%.

To a mixture of 211.0 g. (1.09 moles) of m-phenylenediacetic acid and thionyl chloride (600 g., 5.0 moles) was added 1 ml. of dried dimethylformamide. After stirring at room temperature for 2 hr., the reaction was heated in an oil bath held at 80-85° for 24 hr. The excess thionyl chloride was removed by vacuum distillation. Benzene was added and distilled to remove residual thionyl chloride. The light brown oil was then heated to 50° and vacuum pumped at 0.01 mm. for 1 hr. Further purification of the 244 g. of crude m-phenylenediacetyl chloride was not attempted. The infrared spectrum is shown in Figure 73.

The crude acid chloride was dissolved in 600 ml. of benzene and added under anhydrous conditions to a slurry of 340 g. of modified aluminum chloride (equilibrated 10:1 weight ratio of $AlCl_3$ to $AlCl_3 \cdot 6H_2O$) in 500 ml. of benzene. The reaction was maintained at 20-25° during addition, then heated with stirring at 50° for 18 hr. The reaction mixture was then cooled to room temperature and poured into a mixture of 3 lb. of ice and 500 ml. of concentrated hydrochloric acid. The benzene layer was separated and washed twice with aqueous sodium carbonate, three times with water, and dried over calcium sulfate. Evaporation of the solvent in vacuo left a dark brown oil which crystallized on standing. The solid was triturated with petroleum ether (b.p. 30-60°) and recrystallized from ethyl acetate and finally from ethanol to afford 213 g. (62%) of 1,3-bis(phenylacetyl)-benzene, m.p. 92.5-94° (reported m.p. 90.5-91°) (Ref. 16). The infrared spectrum is shown in Figure 74.

A solution of 76 g. (0.24 mole) of 1,3-bis(phenylacetyl)benzene and 128 g. (0.72 mole) of p-nitroso-N,N-diethylaniline in 1,200 ml. of ethanol was refluxed for 5 hr. The ethanol was evaporated in vacuo and the brown residue then refluxed with 500 ml. of 6N hydrochloric acid for 0.5 hr. After standing at room temperature overnight, the acid was decanted and the residue dissolved in hot ethanol. The solution was treated with decolorizing charcoal and filtered. On cooling, a fluffy yellow solid precipitated. After two additional recrystallizations from ethanol, 40.7 g. (49%) of 1,3-bis(phenylglyoxaloyl)benzene was obtained, m.p. 100.5° (reported m.p. 98-99.5°) (Ref. 16).

Another preparation with 132.0 g. (0.42 mole) of 1,3-bis(phenylacetyl)-benzene gave 71.0 g. (49%) of product, m.p. 101°.

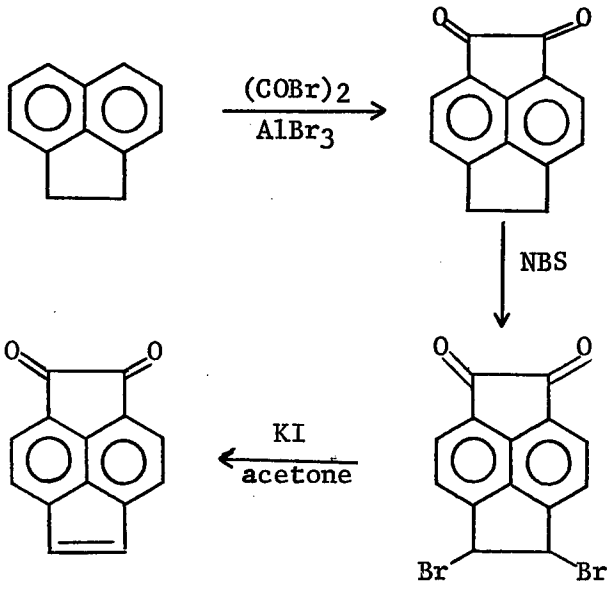
2. Physical properties: 1,3-Bis(phenylglyoxaloyl)benzene was a yellow solid, m.p. 100.5°. Its infrared spectrum is reported in Figure 75.

3. Purity: An elemental analysis of the compound indicated the purity to be 99+%.

Anal. Calcd. for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 77.47; H, 4.12.

M. Pyracyloquinone

This material was prepared via the following three-step reaction sequence (Refs. 18, 19).



A total of 42 g. of pyracen-1,2-dione was prepared from freshly sublimed acenaphthene, and subsequently converted to 37 g. of 5,6-dibromo-1,2-diketopyracene. Although elemental analysis of the dibromide was acceptable, thin-layer chromatography (TLC) showed the presence of two contaminating materials. After recrystallization from carbon tetrachloride and chloroform, 19 g. of dibromide was obtained which was pure by TLC. An 8-g. sample of dibromide was then debrominated to pyracyloquinone. Repeated recrystallization of this material gave a sample which showed acceptable melting characteristics and infrared and NMR spectral data. However, the elemental analysis consistently exceeded permissible limits and indicated the presence of bromine.

1. Synthesis: A solution of 11.9 g. (0.077 mole) of freshly sublimed acenaphthene in 230 ml. of carbon disulfide was cooled to -10°. (Cooling bath consisted of 1:2.5 methanol:water solution with dry ice.) Oxalyl bromide (25 g., 0.116 mole) was then added. The solution was cooled to -20°, and 37.1 g. (0.139 mole) of aluminum bromide was added over 1 hr. A black precipitate formed immediately on addition of the aluminum bromide.

The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. After refluxing for 1 hr. on a hot water bath, the reaction mixture was cooled and the carbon disulfide decanted from the black residue. The residue was treated with 230 ml. of cold 6N hydrochloric acid and was stirred until the evolution of hydrogen bromide ceased. The mixture was filtered and the filter cake was washed with water.

The brown solid was slurried with 400 ml. of 10% sodium bisulfite for 2 hr. at 80° and gravity filtered while hot. The filtrate was heated to 80° and treated with concentrated hydrochloric acid until the evolution of sulfur dioxide ceased. A fluffy yellow precipitate formed. The mixture was stirred an additional 30 min. at 80°, then cooled and filtered. The solid was washed with 25 ml. of cold water.

The sodium bisulfite extraction was then repeated five times on the brown reaction product to give a total of 4.1 g. of yellow solid. After recrystallization from dimethylformamide, 2.8 g. (13%) of pyracen-1,2-dione was obtained, m.p. 306-307° d. (reported m.p. 294-298° d.) (Ref. 19). Infrared spectrum is shown in Figure 76.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.77; H, 3.80. Found: C, 80.59; H, 3.78.

Two additional runs on a 0.65 mole scale gave a total of 40 g. of pyracen-1,2-dione with an average yield of 15%.

A solution of 41.6 g. (0.2 mole) of pyracen-1,2-dione in 4 liters of carbon tetrachloride was refluxed for 30 min. under a nitrogen atmosphere. N-Bromosuccinimide (NBS) (100.4 g., 0.6 mole) and 4.0 g. of benzoyl peroxide were added to the hot solution and the mixture was refluxed for 5 hr. The reaction mixture was filtered hot, and the filter cake washed with an additional liter of carbon tetrachloride. The combined filtrates were evaporated in vacuo to afford a dark yellow solid which was washed with methanol to remove residual succinimide. Recrystallization from carbon tetrachloride afforded 37.0 g. (50.8%) of 5,6-dibromo-1,2-diketopyracene which decomposed on melting at 192-193.5° d. (reported m.p. 189-193° d.) (Ref. 19).

Anal. Calcd. for $C_{14}H_6O_2Br_2$: C, 45.94; H, 1.65. Found: C, 45.51; H, 1.60.

Thin-layer chromatography (TLC) of the compound on silica gel with chloroform:carbon tetrachloride (60:40) showed the presence of two contaminating materials. Recrystallization of the material from carbon tetrachloride and from chloroform afforded 19.0 g. of product. The melting point was elevated to 203.5-205° d. (192-194° d. via differential thermal analysis). TLC showed only one component. The infrared spectrum is reported in Figure 77.

Anal. Calcd. for $C_{14}H_6O_2Br_2$: C, 45.94; H, 1.65; Br, 43.66. Found: C, 45.47; H, 1.57; Br, 43.89.

A solution of 8.0 g. (0.022 mole) of 5,6-dibromo-1,2-diketopyracene in 600 ml. of acetone was heated with 50.0 g. (0.30 mole) of anhydrous

potassium iodide at reflux temperatures for 5 hr. After cooling to room temperature, the mixture was poured into a cooled aqueous sodium thiosulfate solution. The aqueous mixture was then extracted with chloroform. Evaporation of chloroform afforded a red solid which was recrystallized from ethanol to give 3.5 g. of pyracyloquinone (III), m.p. > 400° (reported m.p. > 400°) (Ref. 19). A Beilstein test for halogen was positive.

Anal. Calcd. for $C_{14}H_6O_2$: C, 81.54; H, 2.93. Found: C, 77.95; H, 2.69.

The product was recrystallized an additional two times from ethanol to afford 2.3 g. (51%) of pyracyloquinone.

2. Physical properties: Pyracyloquinone was a red powder, m.p. > 400°.

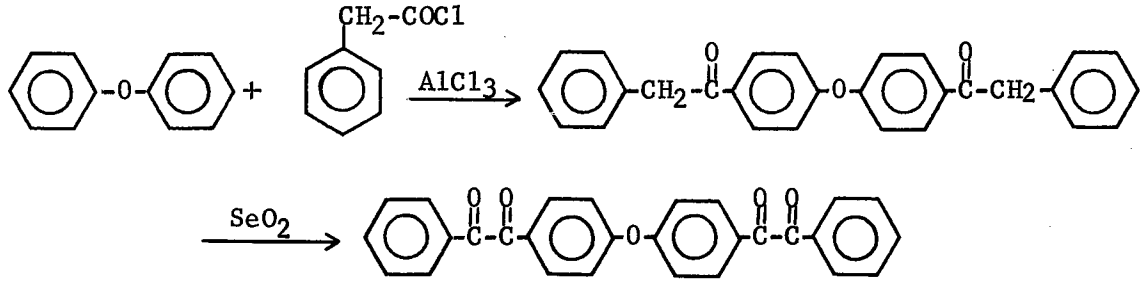
3. Purity: Infrared and NMR spectral data were consistent with the structure and corresponded to reported literature values (Ref. 19). (See Figures 78 and 79.) TLC on silica gel with chloroform:carbon tetrachloride (60:40) showed one component. A careful examination for the presence of unreacted 5,6-dibromo-1,2-diketopyracene indicated none present. An elemental analysis, however, exceeded permissible limits and showed the presence of bromine.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 81.54; H, 2.93. Found: C, 82.59; H, 3.29; Br, 0.32.

If the bromine is attributed to the dehydrobrominated product, 5-bromopyracycloquinone, the purity of the sample based on elemental analysis was 98.9%.

N. p,p'-Oxydibenzil

This material was prepared by the procedures described by Hergenrother (Ref. 20).



1. Synthesis: A solution of diphenylether (55 g., 0.323 mole) and phenylacetyl chloride (100 g., 0.65 mole) in 165 ml. of methylene chloride was added under anhydrous conditions to a stirred mixture of 86.0 g. of modified aluminum chloride (10:1 weight ratio of $AlCl_3$ and $AlCl_3 \cdot 6H_2O$) in 485 ml. of methylene chloride. The reaction mixture was held at 15-20° during addition, then stirred at room temperature for 18 hr. The brown reaction mixture was poured into a mixture of 400 g. of ice with 125 ml. of concentrated hydrochloric acid. The organic phase was separated and washed successively with water, aqueous sodium bicarbonate, and water followed by drying over anhydrous magnesium sulfate. Concentration to about 150 ml. followed by cooling provided 59.0 g. of cream-colored solid. The material was recrystallized from benzene to afford 57.7 g. (44%) of p,p'-di(phenylacetylphenyl) ether, m.p. 168-169° (Reported m.p. 169-170°) (Ref. 20). The infrared spectrum is reported in Figure 80.

A second preparation on the same scale gave 57.0 g. (44%) of additional product.

To a mixture of 11.1 g. (0.1 mole) of selenium dioxide in 150 ml. of glacial acetic acid at 60° was added 20.0 g. (0.05 mole) of p,p'-di(phenylacetylphenyl) ether. The reaction mixture was then refluxed for 24 hr. The mixture was filtered hot, and the filtrate concentrated to about 75 ml. and cooled to provide a yellow solid. The solid was washed with methanol and recrystallized twice from a mixture of ethyl acetate and n-hexane to afford 15.5 g. (72%) of p,p'-oxydibenzil, m.p. 104-105.5° (reported m.p. 108-109°) (Ref. 20).

Another preparation on a 0.23 mole scale gave 84.2 g. (84%) of additional p,p'-oxydibenzil.

2. Physical properties: p,p'-Oxydibenzil was a light yellow powder, m.p. 104-105.5°. Its infrared spectrum is reported in Figure 81.

3. Purity: Elemental analysis of the compound indicated the purity to be 99+%.

Anal. Calcd. for $C_{28}H_{18}O_5$: C, 77.41; H, 4.18. Found: C, 77.68; H, 4.15.

III.

SAMPLE SHIPMENTS

Samples of compounds which were shipped during this report period are listed as follows:

Benzidine 3,3'-dicarboxylic acid (Sample 1)	114.0 g.
Benzidine 3,3'-dicarboxylic acid (Sample 2)	108.0 g.
Benzidine 3,3'-dicarboxylic acid (Sample 3)	38.0 g.
Diethyl 2,5-diaminoterephthalate	44.0 g.
Diethyl 2,5-diimino-1,4-cyclohexanedicarboxylate	13.9 g.
Bis(trifluoromethyl)peroxide	10.0 g.
1,3-Di(trifluoromethyl)benzene	100.0 g.
Hexafluoroisopropanol	100.0 g.
Pentafluorophenylphosphonous dibromide	132.7 g.
Perfluoro-1-bromo-4-n-octylbenzene	346.0 g.
Carbon monofluoride (CF_x, where: x = 1.1)	30.0 g.
1,1'-Bis(hydroxymethyl)ferrocene (Sample 1)	1.0 g.
Hydroxymethylferrocene (Sample 1)	1.0 g.
1,1'-Bis(methoxycarbonyl)ferrocene	1.0 g.
1,1'-Bis(carboxy)ferrocene	1.0 g.
Bis(pentafluorophenyl)phosphinous bromide	112.0 g.
1,1'-Bis(hydroxymethyl)ferrocene (Sample 2)	125.0 g.
Bromopentafluorobenzene	1.0 kg.
1,1'-Bis(hydroxymethyl)ferrocene (Sample 3)	225.0 g.
1,4,5,8-Naphthalenetetracarboxylic acid	25.0 g.
1,1'-Bis(formyl)ferrocene (Sample 1)	1.0 g.
Activated MnO_2	15.0 g.
1,1'-Bis(formyl)ferrocene (Sample 2)	203.7 g.
Ruthenocene	119.0 g.
Hexabromobenzene	28.0 g.
Hydroxymethylferrocene (Sample 2)	198.0 g.
1,3-Bis(phenylglyoxaloyl)benzene	110.0 g.
5,6-Dibromo-1,2-diketopyracene	10.0 g.
Pyracyloquinone	2.2 g.
p,p'-Oxydibenzil	98.0 g.

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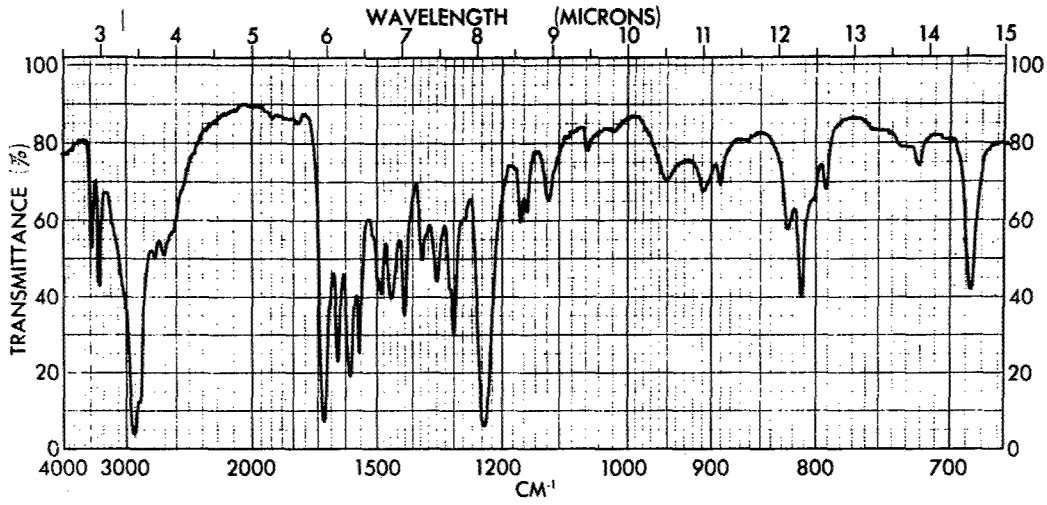


Figure 1 - Infrared Spectrum of the Benzidine 3,3'-Dicarboxylic Acid Sample (Nujol)

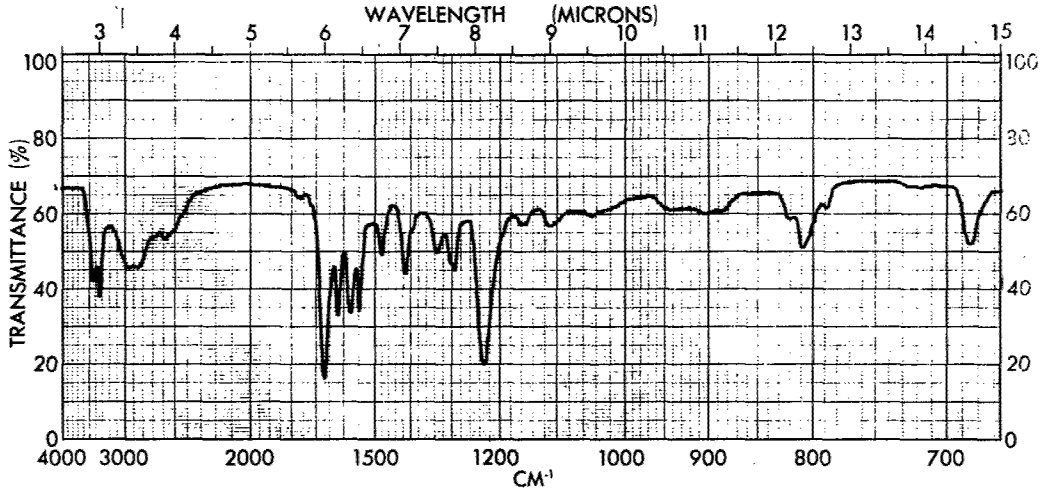


Figure 2 - Infrared Spectrum of Benzidine 3,3'-Dicarboxylic Acid Derived from the Commercial Material (KBr)

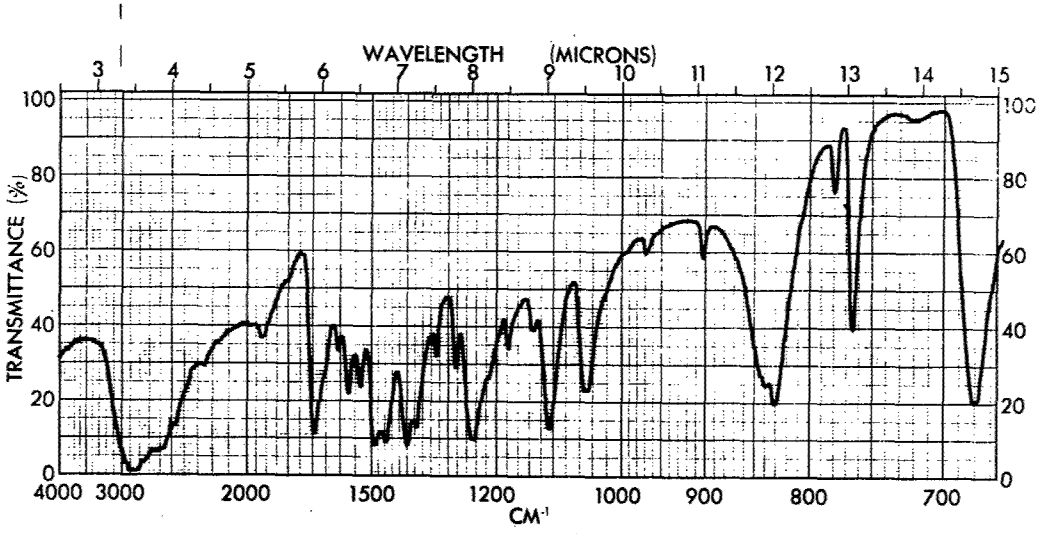


Figure 3 - Infrared Spectrum of Benzidine 3,3'-Dicarboxylic Acid Dihydrochloride Derived from the Commercial Material (Nujol)

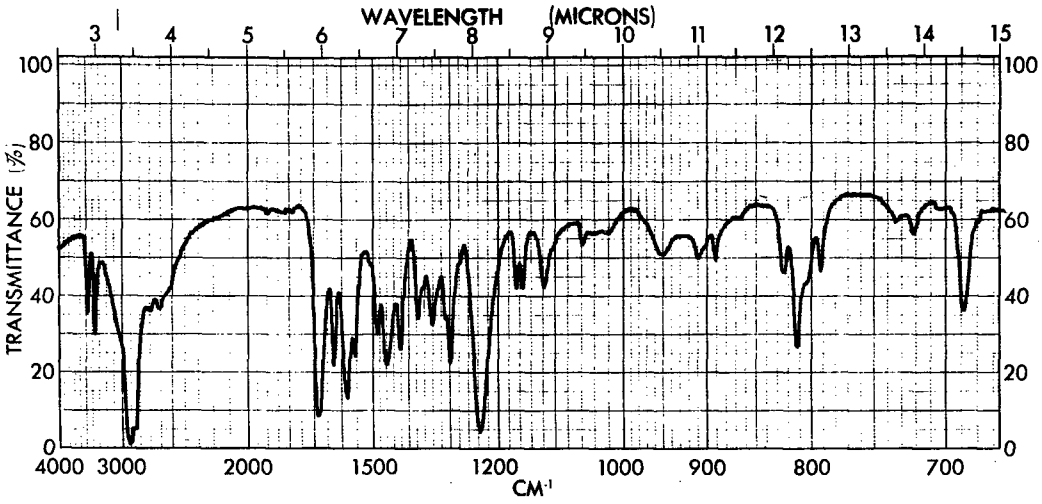


Figure 4 - Infrared Spectrum of the Second Benzidine 3,3'-Dicarboxylic Acid Sample (Nujol)

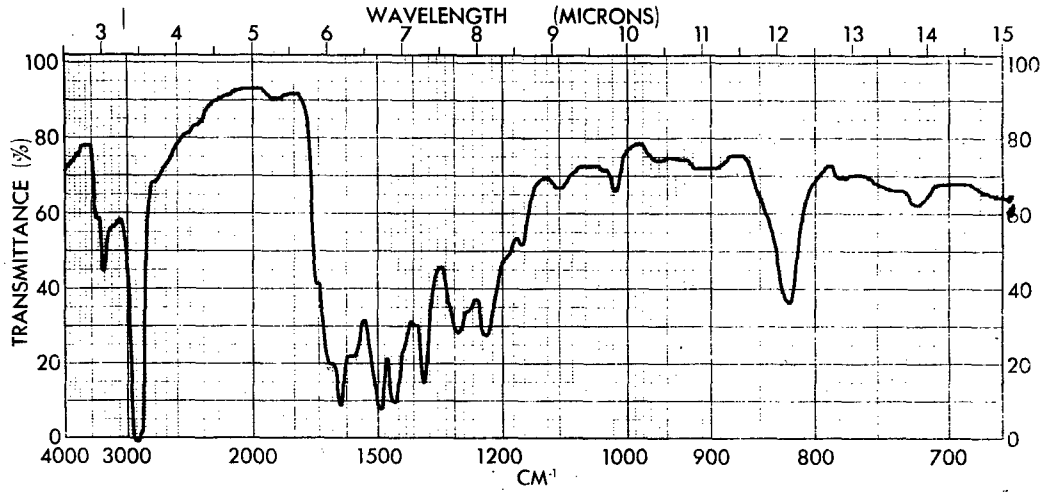


Figure 5 - Infrared Spectrum of the Substance Precipitated from Dimethylacetamide in the "Bisdione" Preparation (Nujol)

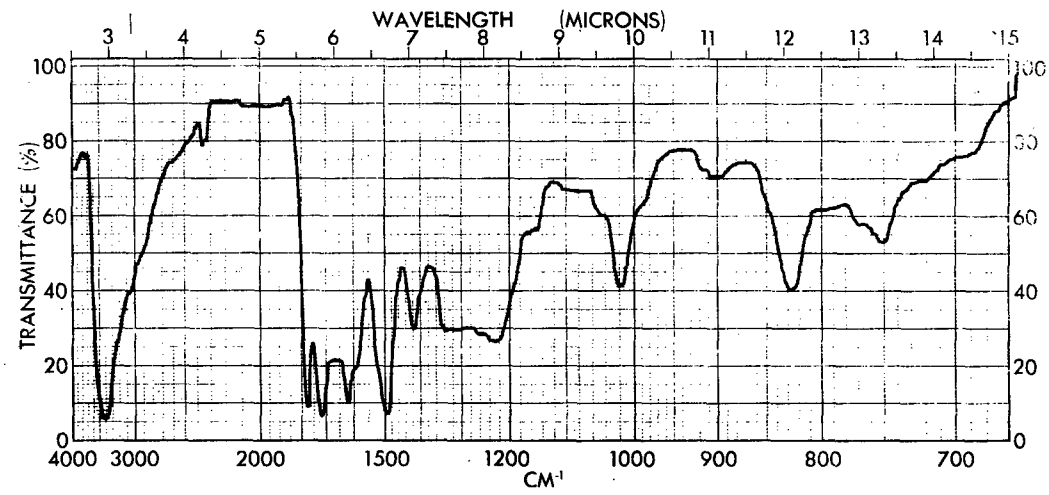


Figure 6 - Infrared Spectrum of Substance Obtained Directly in the "Bisdione" Preparation (KBr)

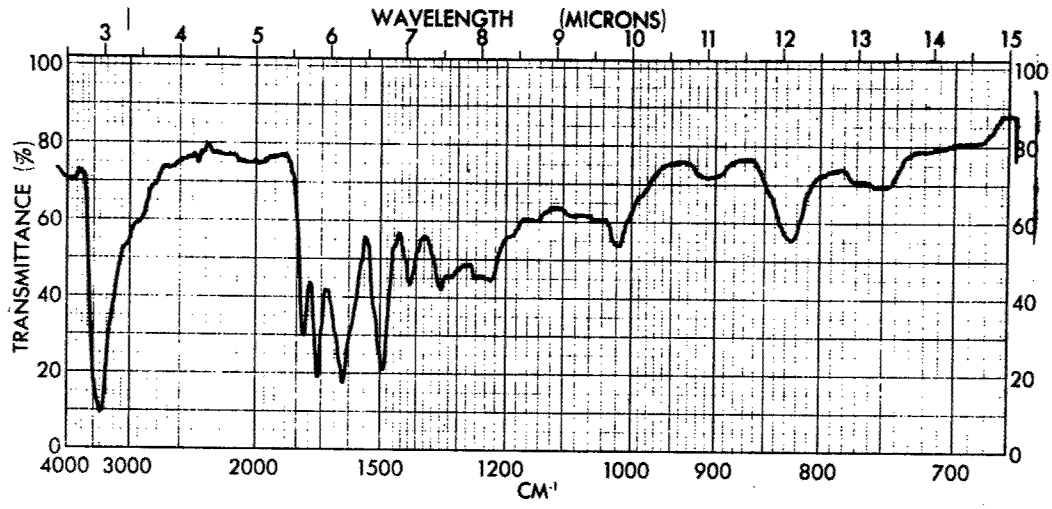


Figure 7 - Infrared Spectrum of the Substance Obtained Directly in the "Bisdione" Preparation from More Highly Purified Benzidine 3,3'-Dicarboxylic Acid (KBr)

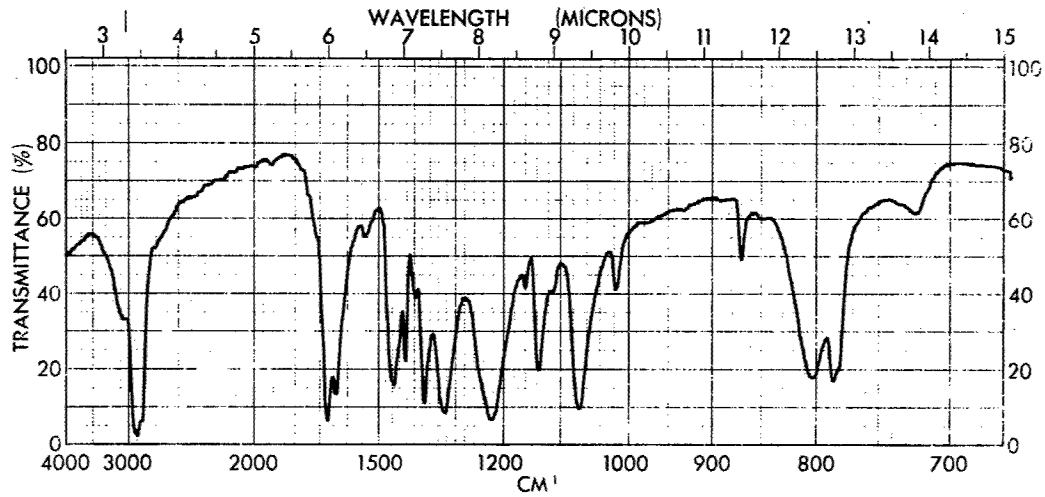


Figure 8 - Infrared Spectrum of Diethyl 2,5-Dioxo-1,4-Cyclohexane-dicarboxylate (Nujol)

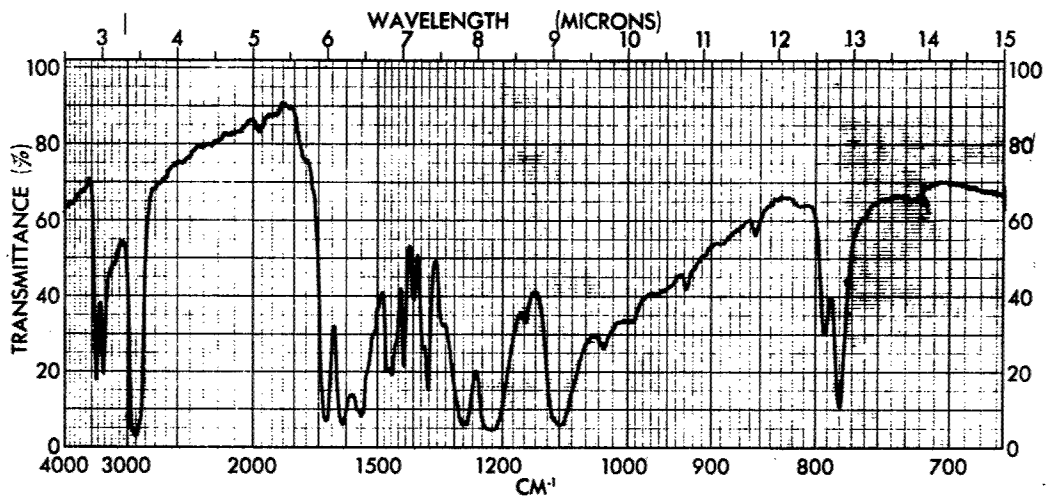


Figure 9 - Infrared Spectrum of Diethyl 2,5-Diimino-1,4-cyclo-hexanedicarboxylate (Nujol)

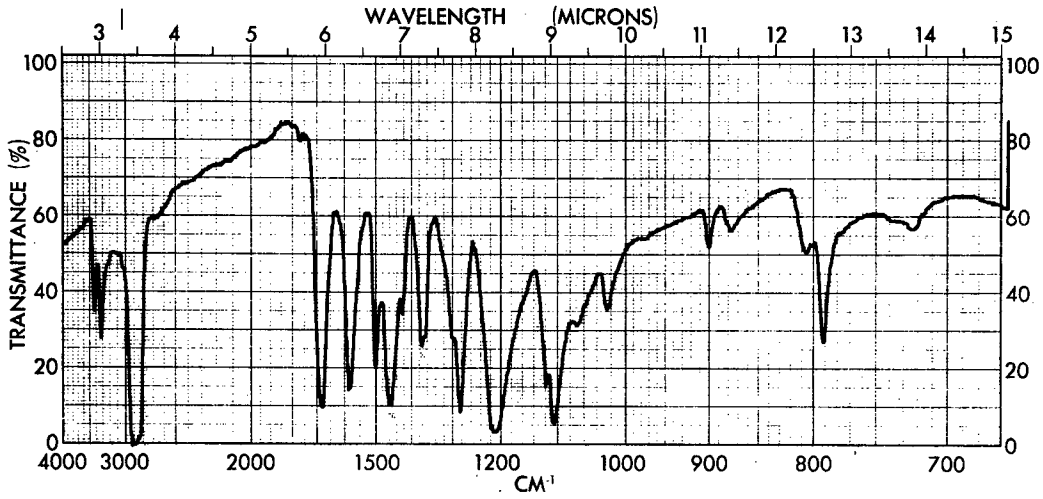


Figure 10 - Infrared Spectrum of the Sample of Diethyl 2,5-Diaminoterephthalate (Nujol)

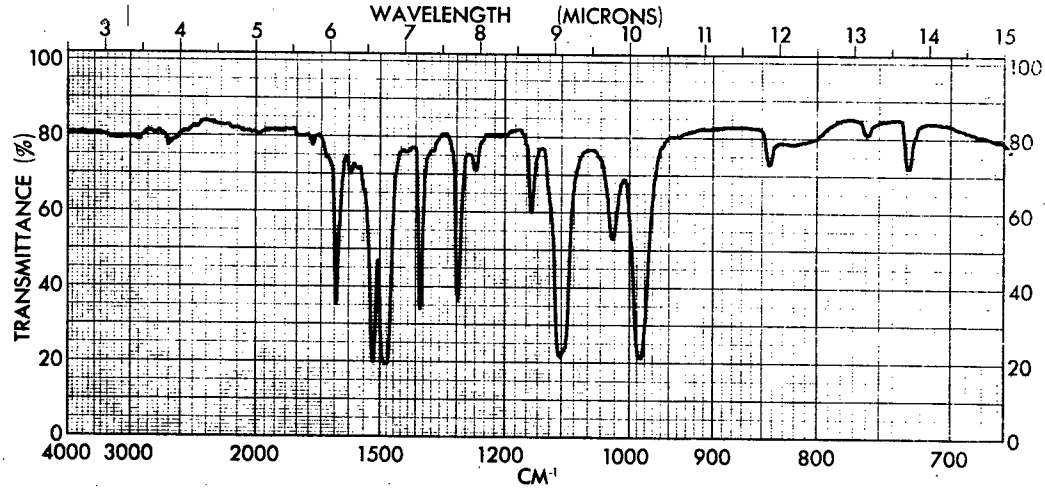


Figure 11 - Infrared Spectrum of Pentafluorophenylphosphonous Dibromide (Liquid)

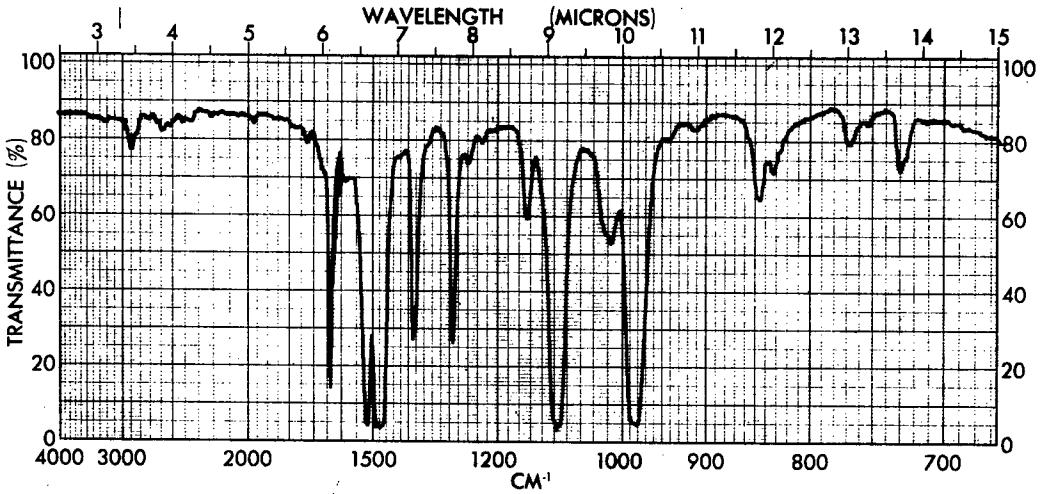


Figure 12 - Infrared Spectrum of Bis(pentafluorophenyl)phosphinous Bromide (Liquid)

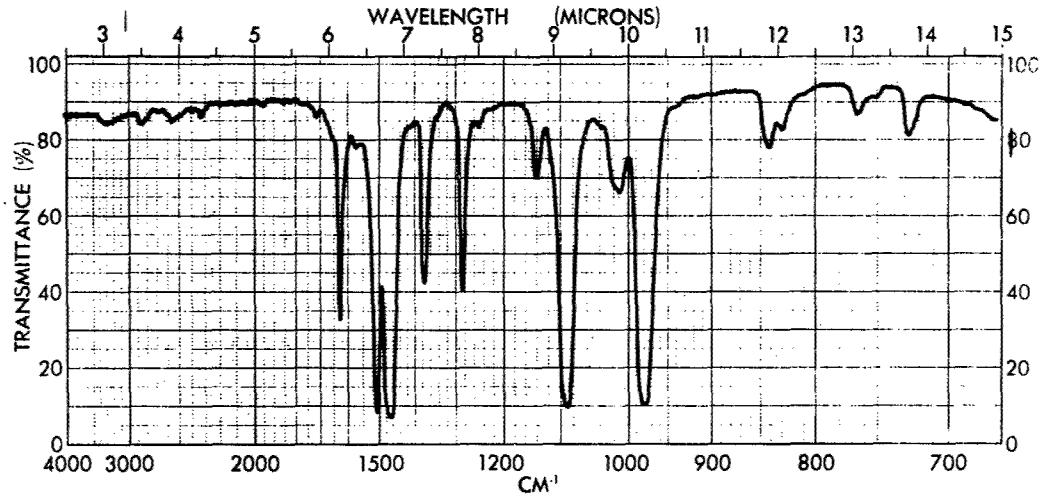


Figure 13 - Infrared Spectrum of Bis(pentafluorophenyl)phosphinous Bromide--Twice Distilled (Liquid)

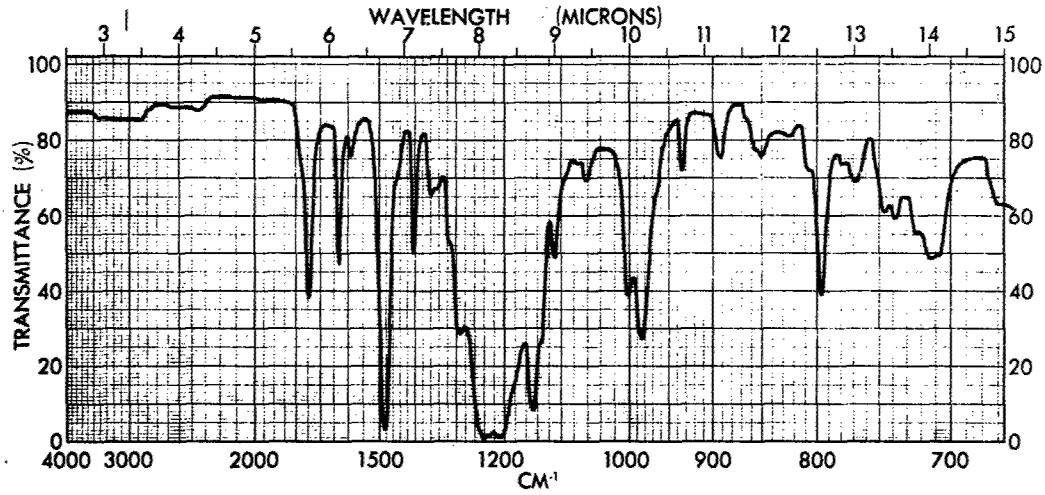


Figure 14 - Infrared Spectrum of 4-Bromoperfluorooctanophenone (Liquid)

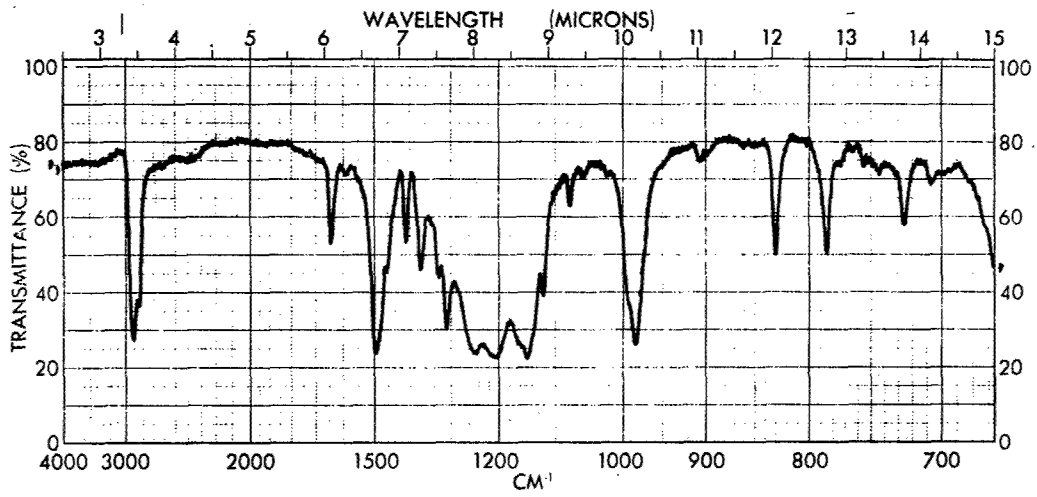


Figure 15 - Infrared Spectrum of Perfluoro-1-bromo-4-n-octylbenzene (Nujol)

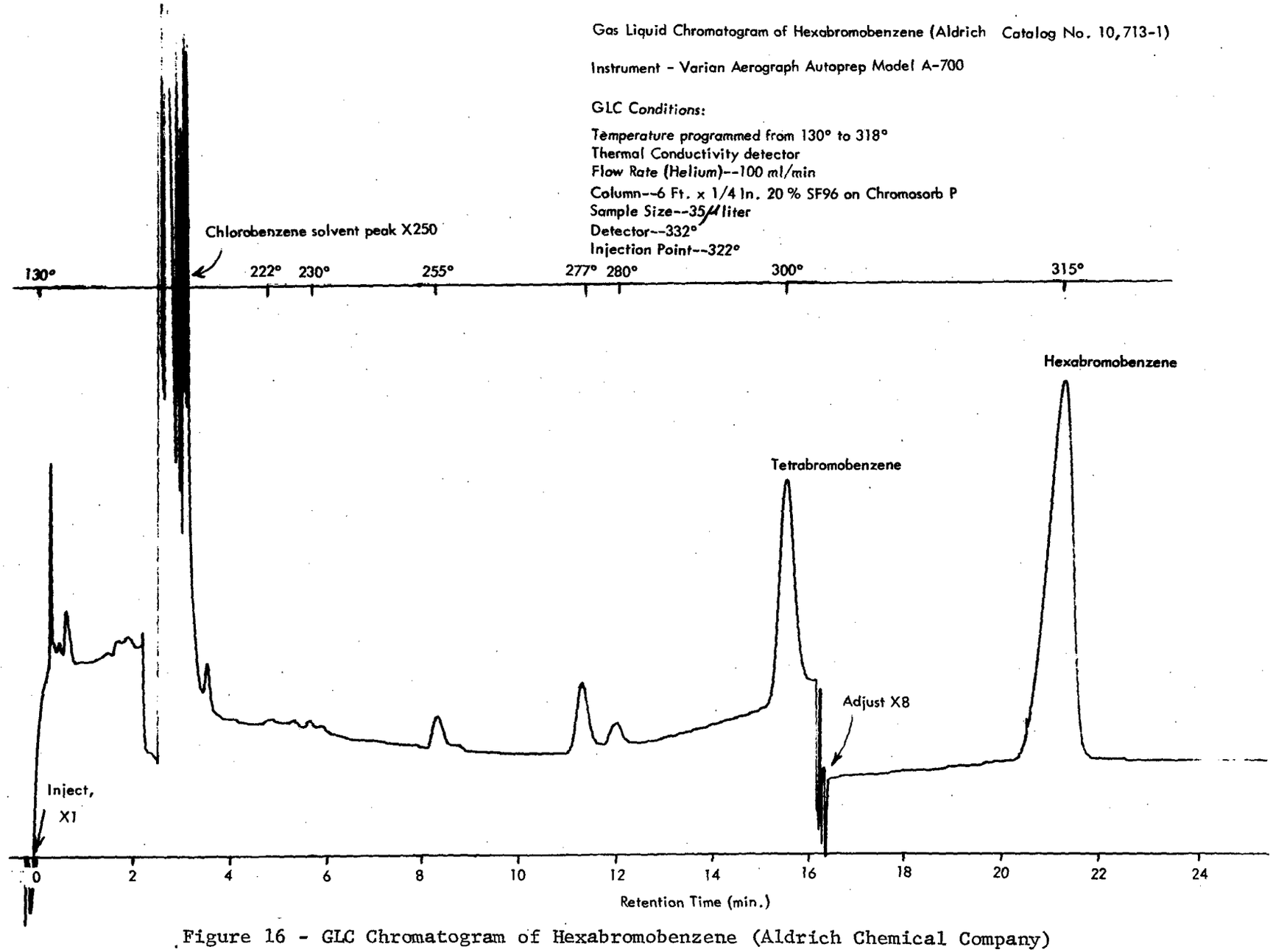


Figure 16 - GLC Chromatogram of Hexabromobenzene (Aldrich Chemical Company)

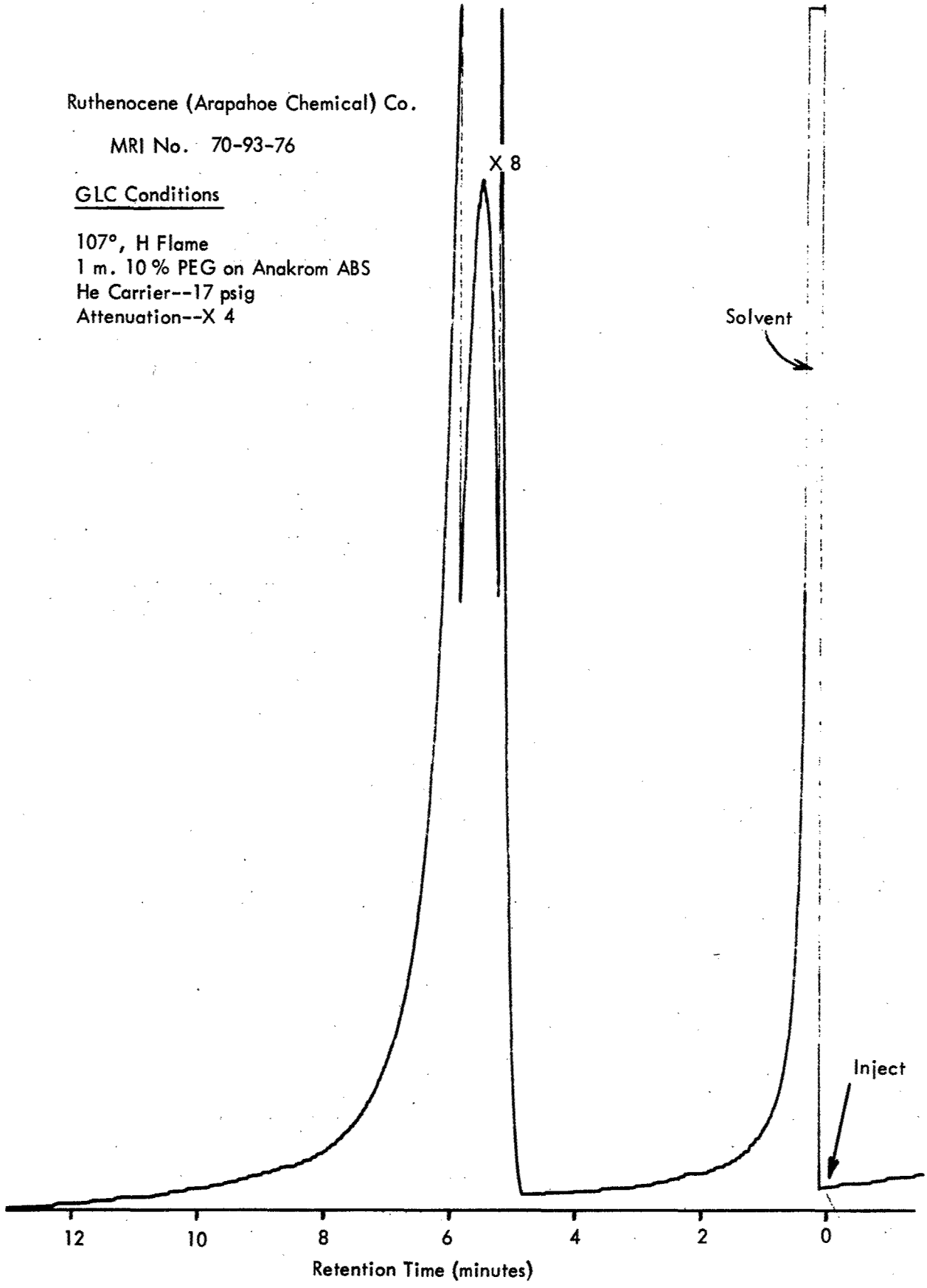


Figure 17 - GLC Chromatogram of Ruthenocene (Arapahoe Chemical Company)

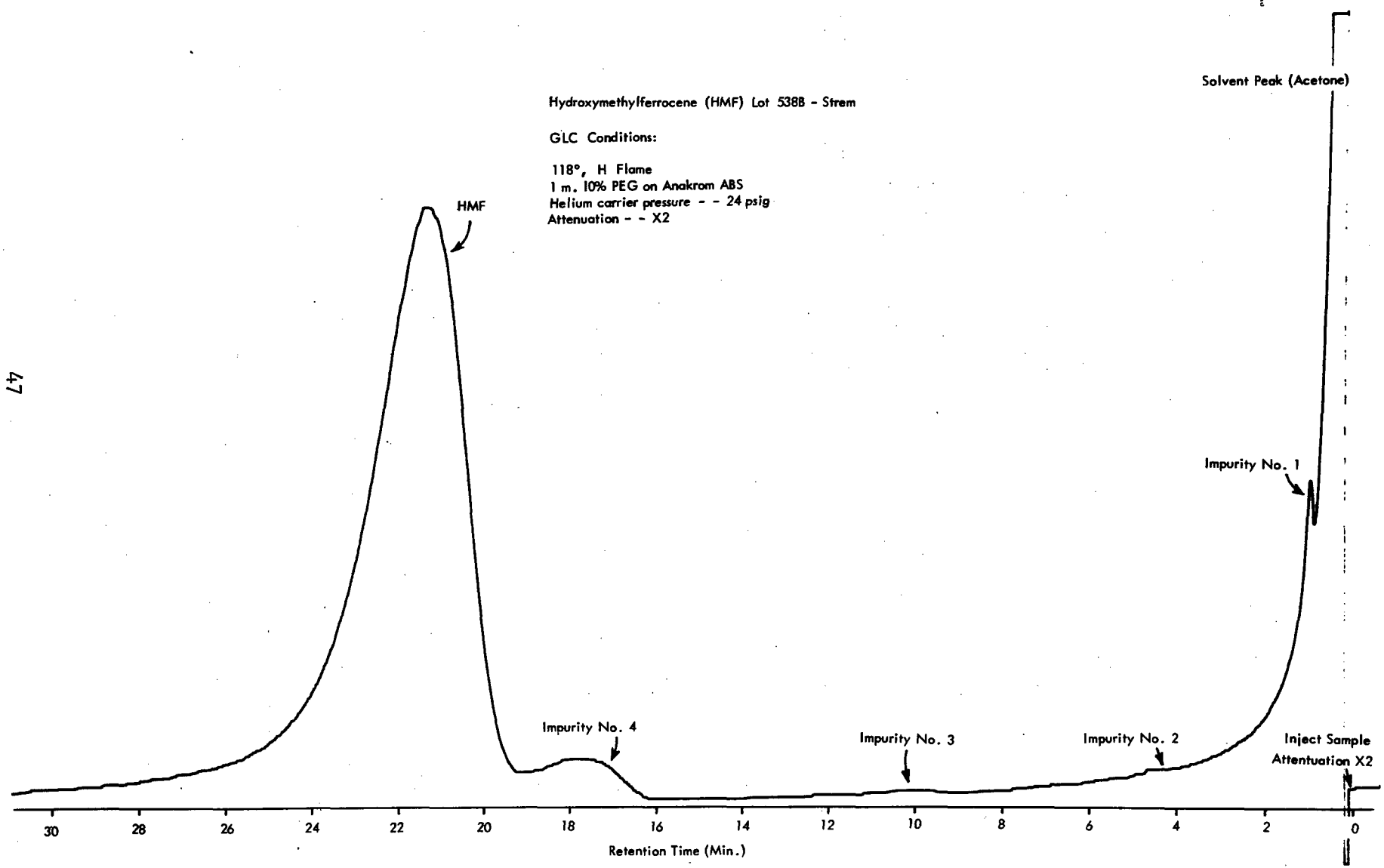


Figure 18 - GLC Chromatogram of Hydroxymethylferrocene (Strem Chemical Company)

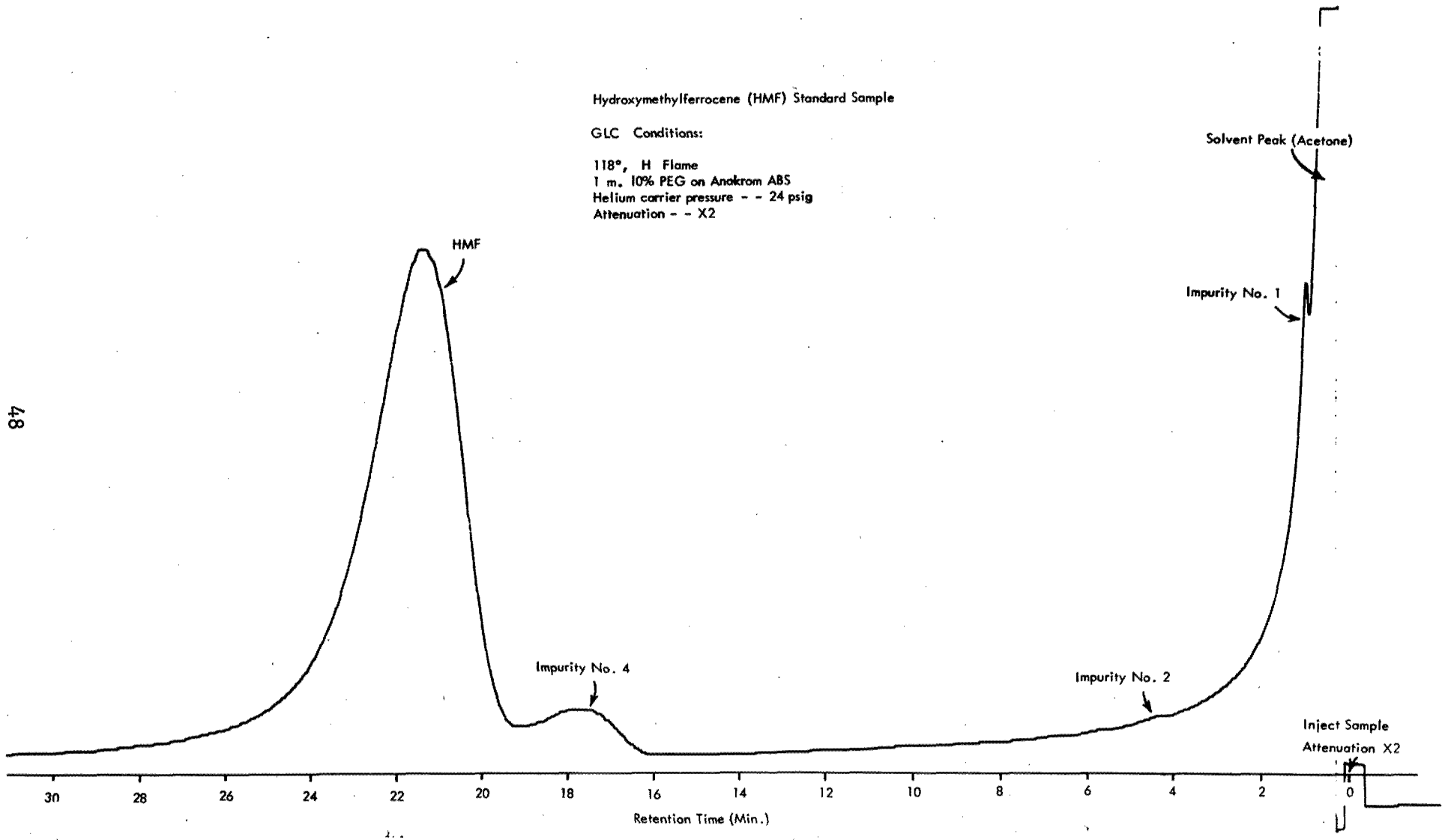


Figure 19 - GLC Chromatogram of Hydroxymethylferrocene (Standard Sample)

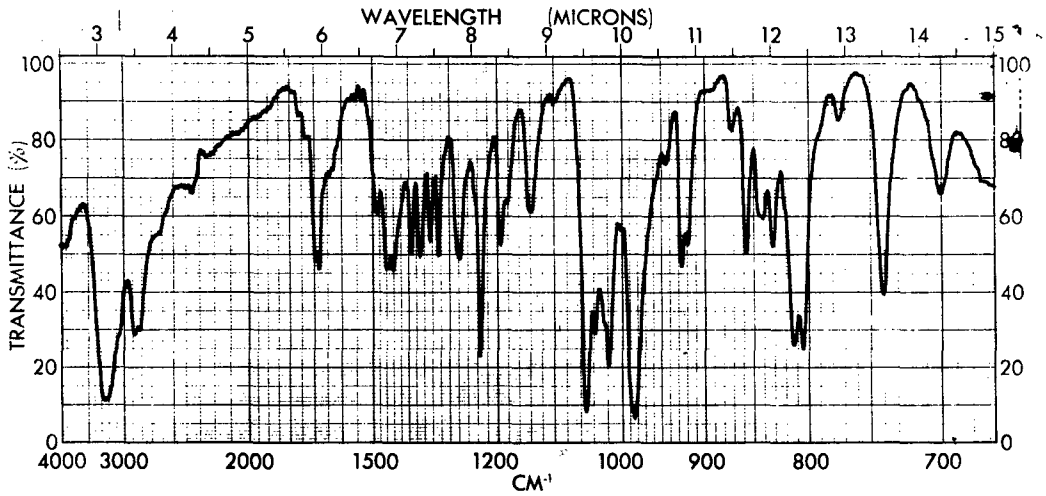


Figure 20 - Infrared Spectrum of 1,1'-Bis(hydroxymethyl)ferrocene (KBr)

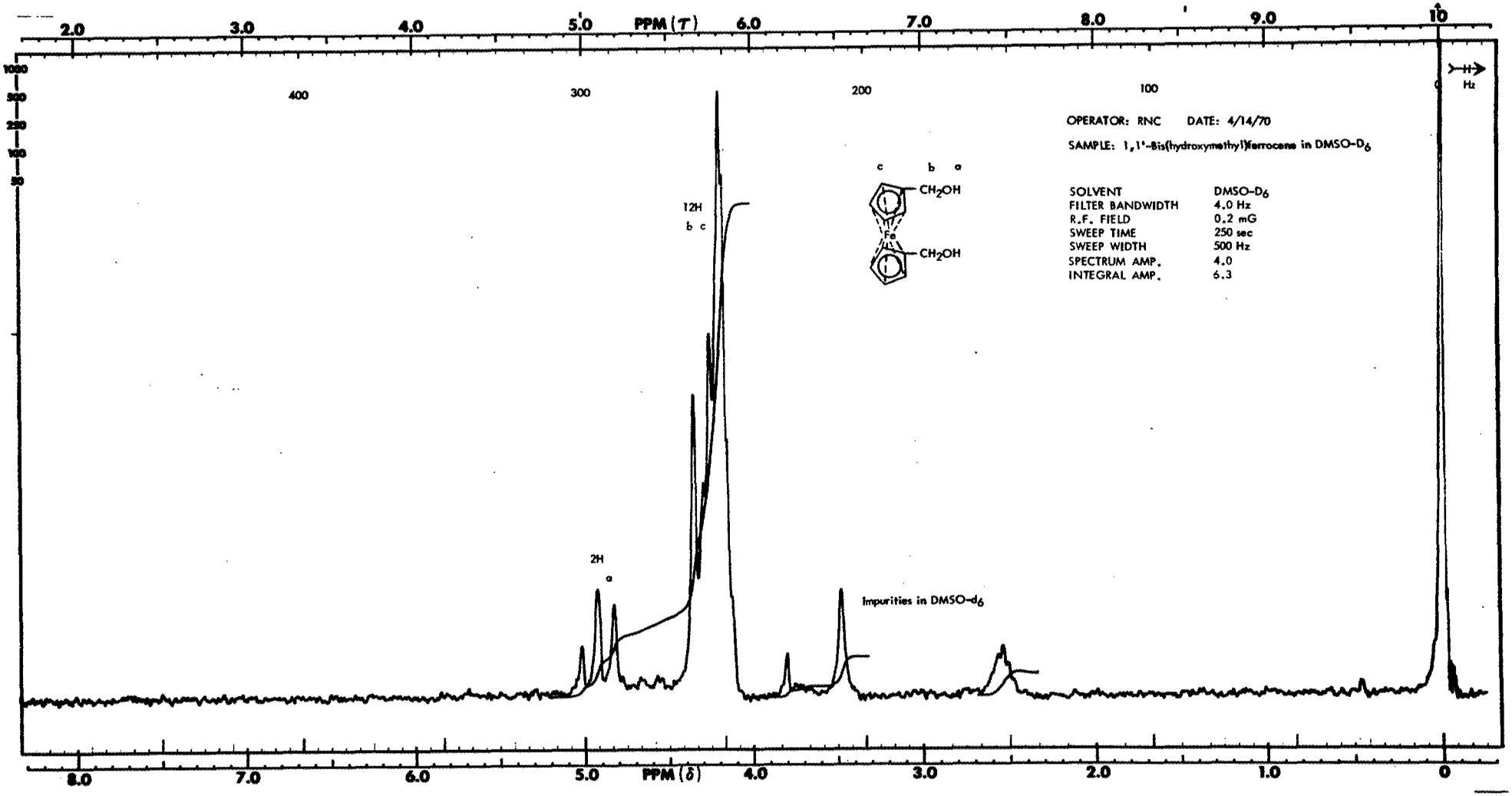


Figure 21 - NMR Spectrum of 1,1'-Bis(hydroxymethyl)ferrocene (in DMSO-d_6)

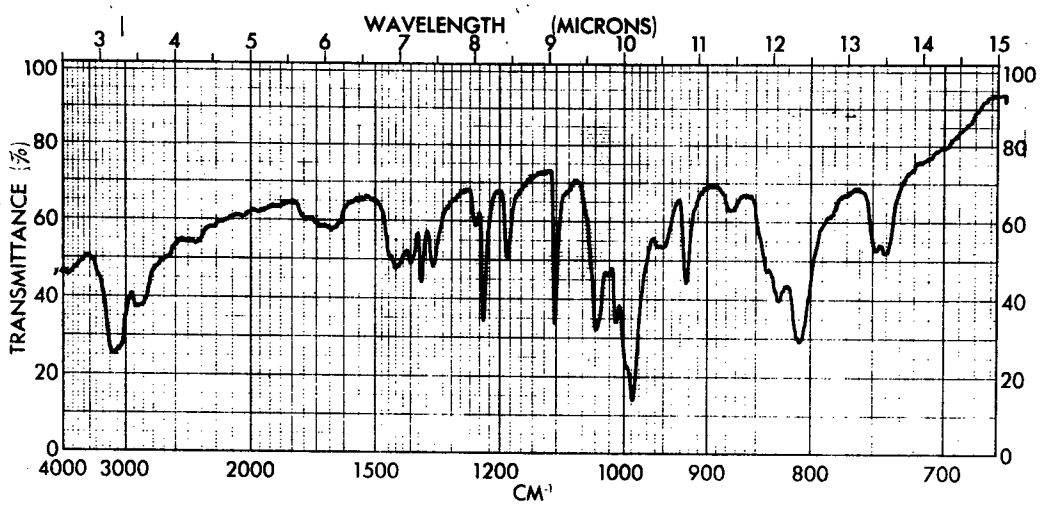


Figure 22 - Infrared Spectrum of Hydroxymethylferrocene (KBr)

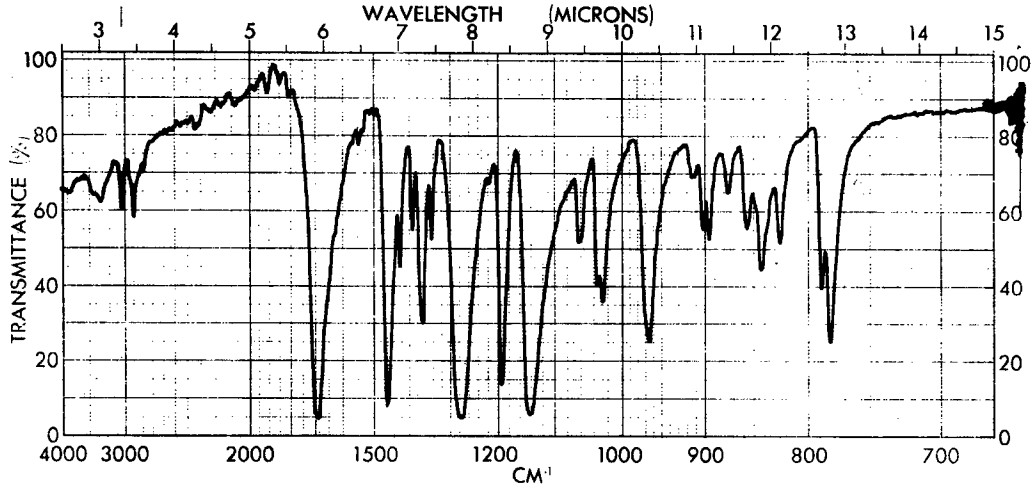


Figure 23 - Infrared Spectrum of 1,1'-Bis(methoxycarbonyl)ferrocene (KBr)

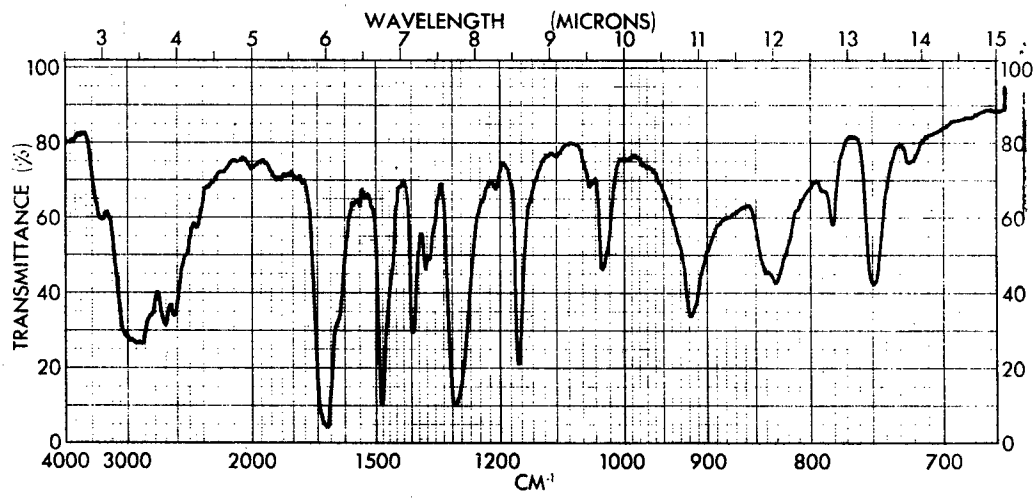


Figure 24 - Infrared Spectrum of 1,1'-Bis(carboxy)ferrocene (KBr)

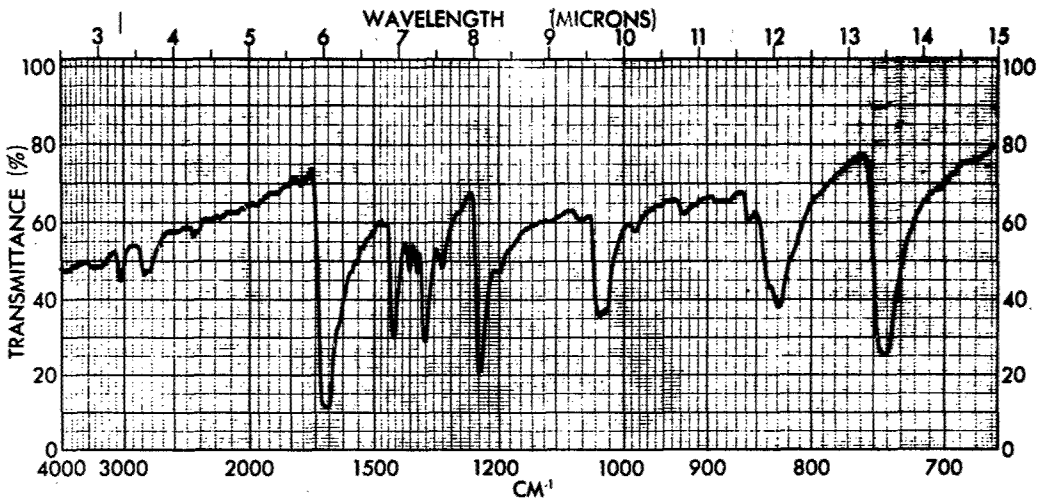


Figure 25 - Infrared Spectrum of 1,1'-Bis(formyl)ferrocene (KBr)

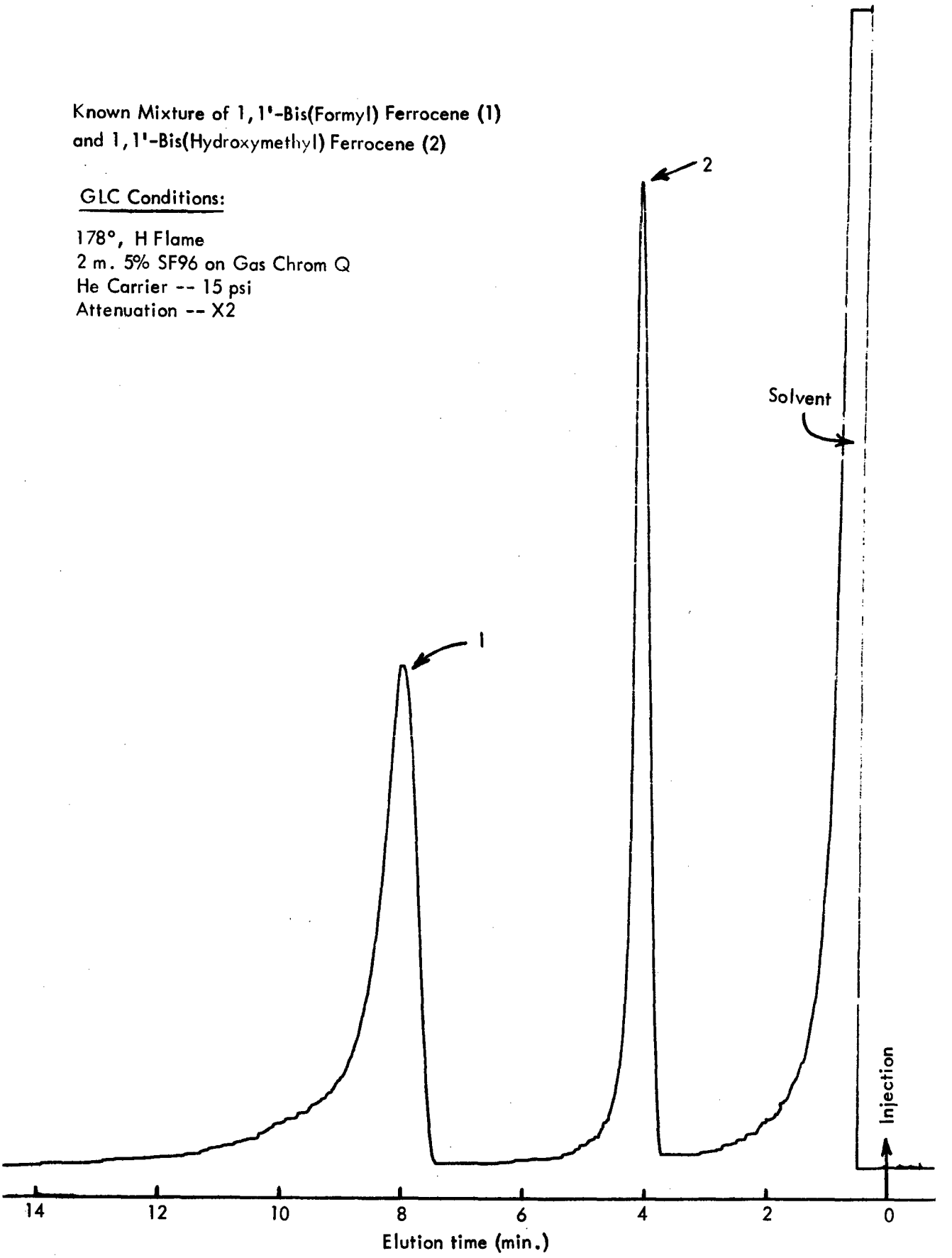


Figure 26 - Gas Liquid Chromatogram of a Mixture of 1,1'-Bis(hydroxymethyl)-ferrocene and 1,1'-Bis(formyl)ferrocene

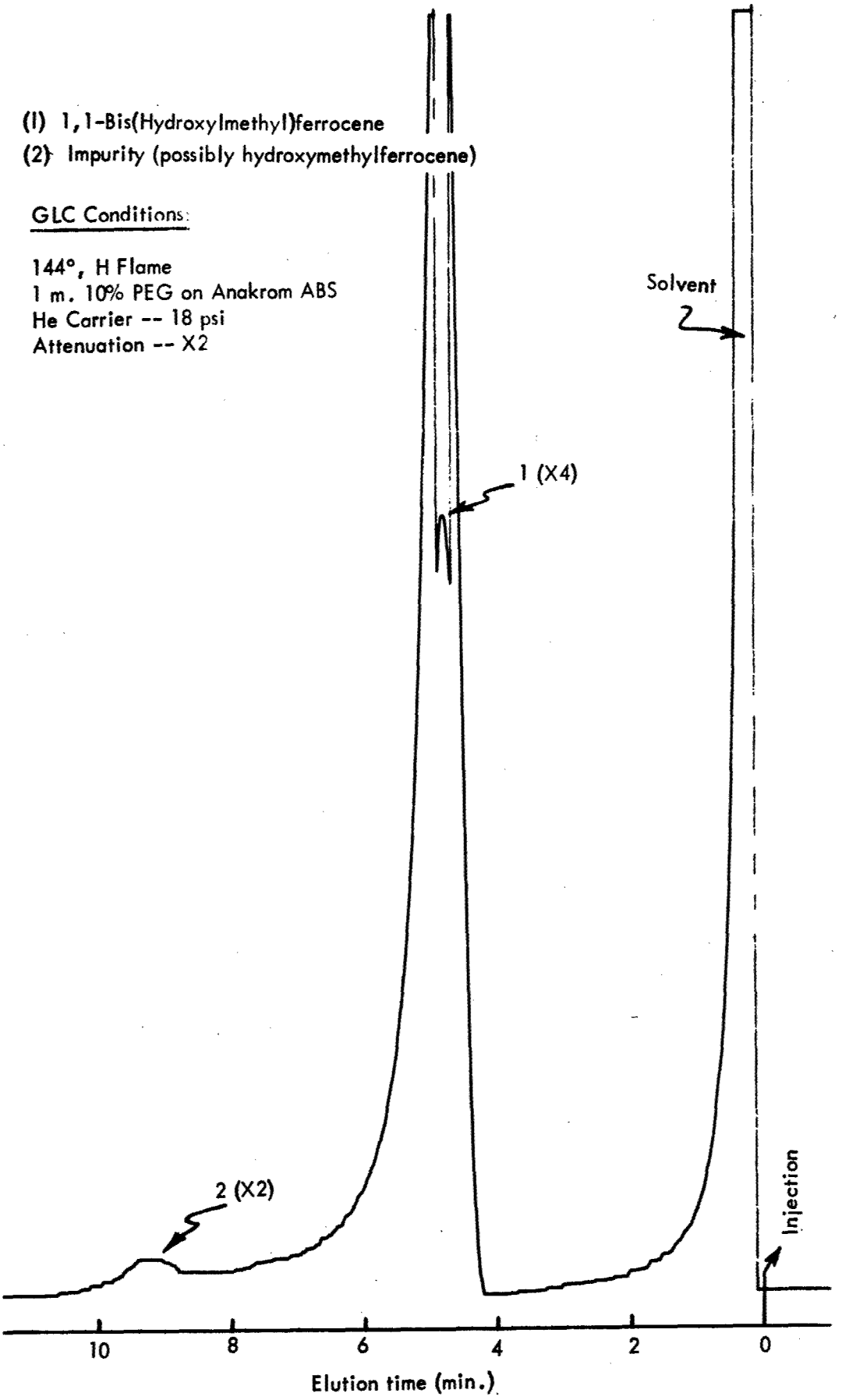


Figure 27 - Gas Liquid Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene

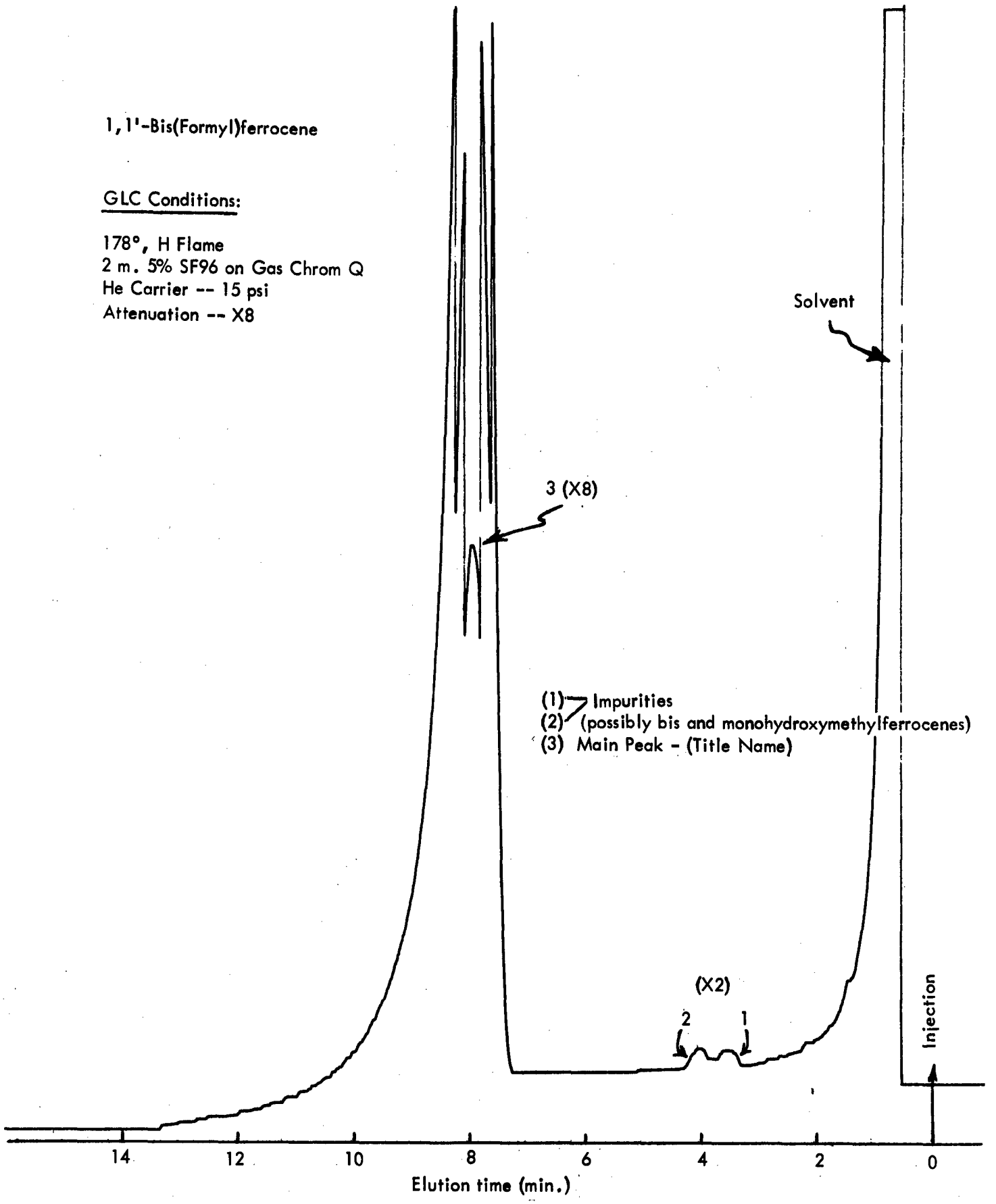


Figure 28 - Gas Liquid Chromatogram of 1,1'-Bis(formyl)ferrocene

Known Mixture of 1,1'-Bis(hydroxymethyl)ferrocene (1) and Hydroxymethylferrocene (2).

GLC Conditions:
178°, H Flame
2 m. 5% SF96 on Gas ChromQ
He Carrier--15 psi
Attenuation--X4

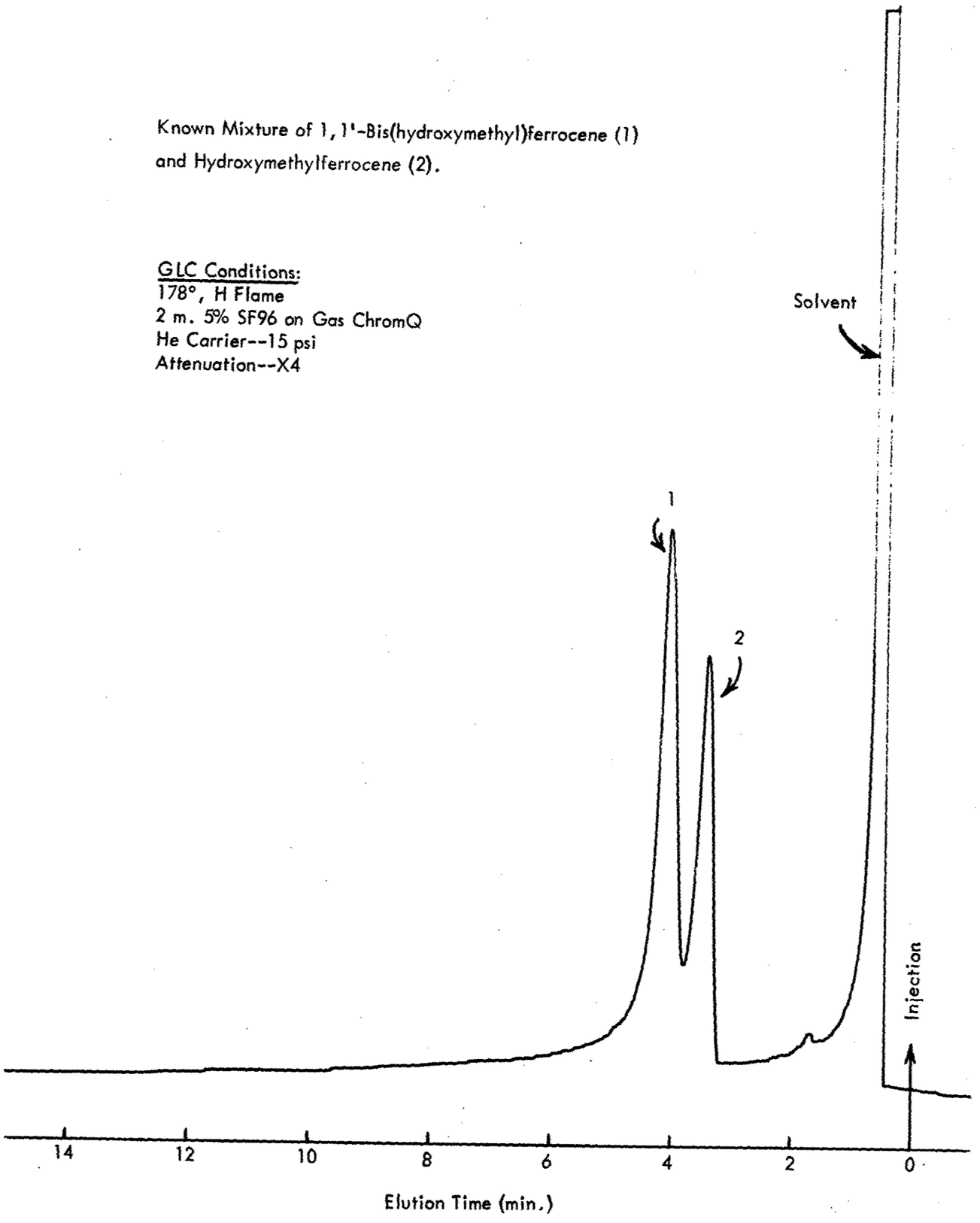


Figure 29 - Gas Liquid Chromatogram of a Mixture of Hydroxymethyl-ferrocene and 1,1'-Bis(hydroxymethyl)ferrocene

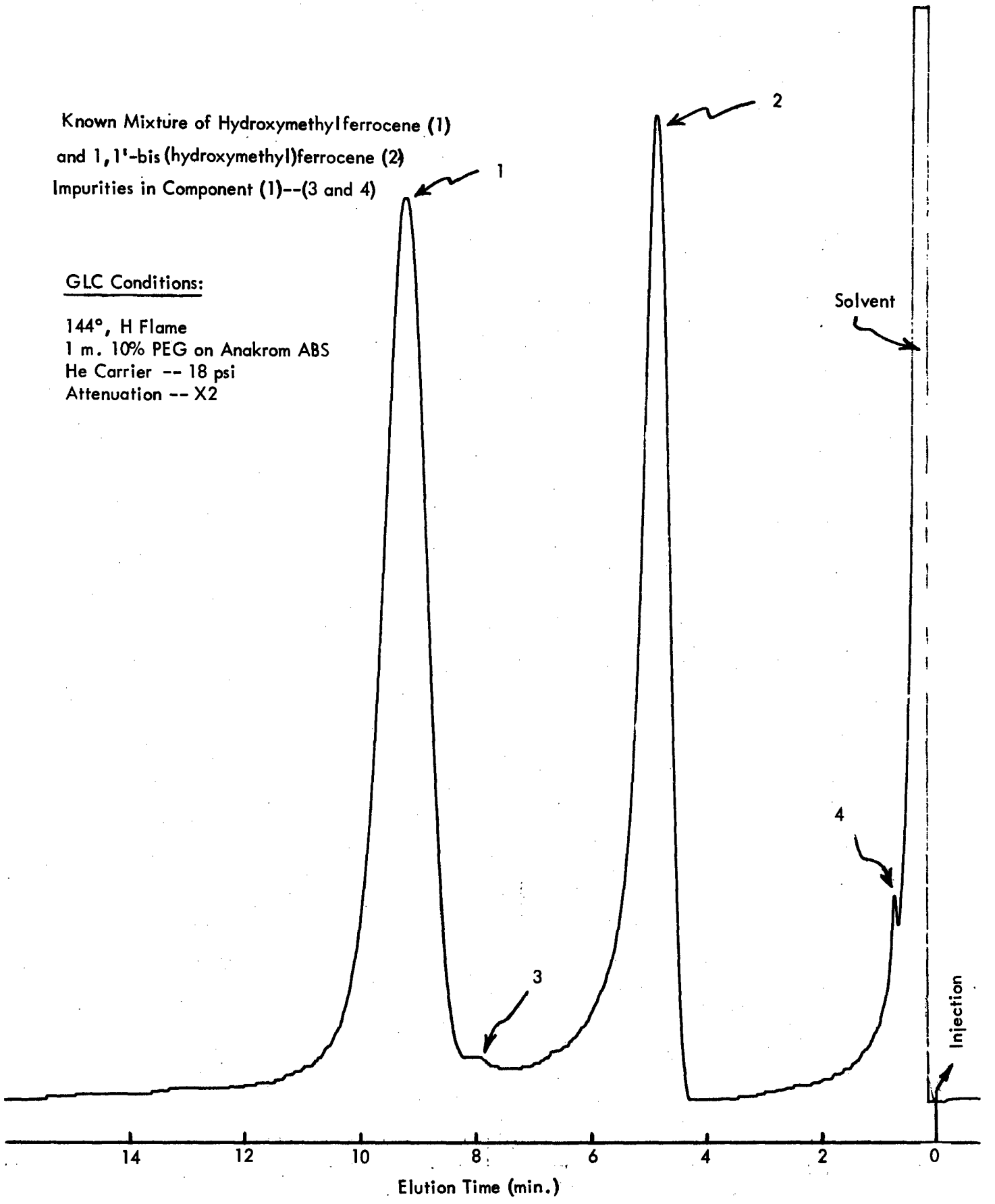


Figure 30 - Gas Liquid Chromatogram of a Mixture of Hydroxymethylferrocene and 1,1'-Bis(hydroxymethyl)ferrocene

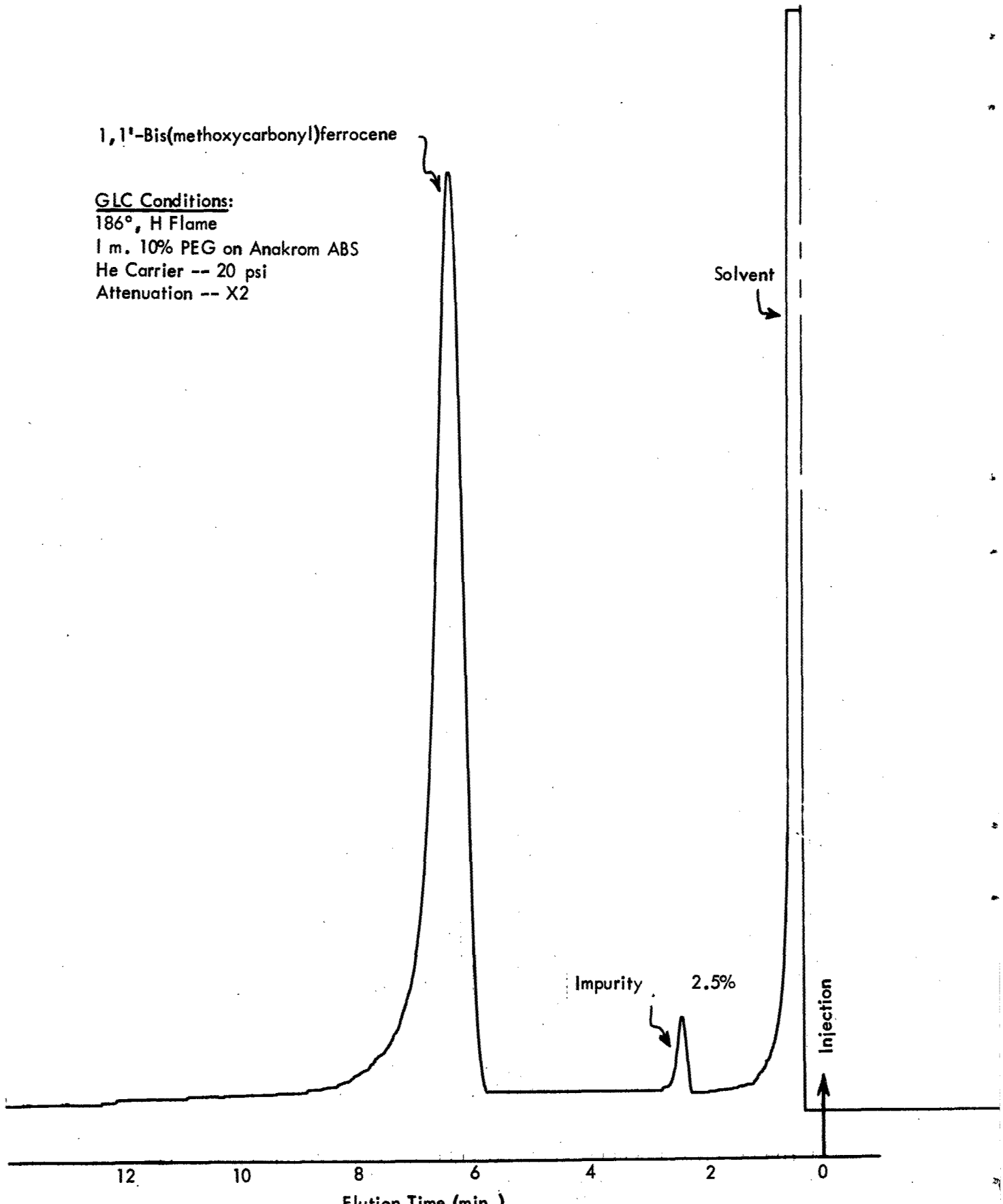


Figure 31 - Gas Liquid Chromatogram of 1,1'-Bis(methoxycarbonyl)ferrocene

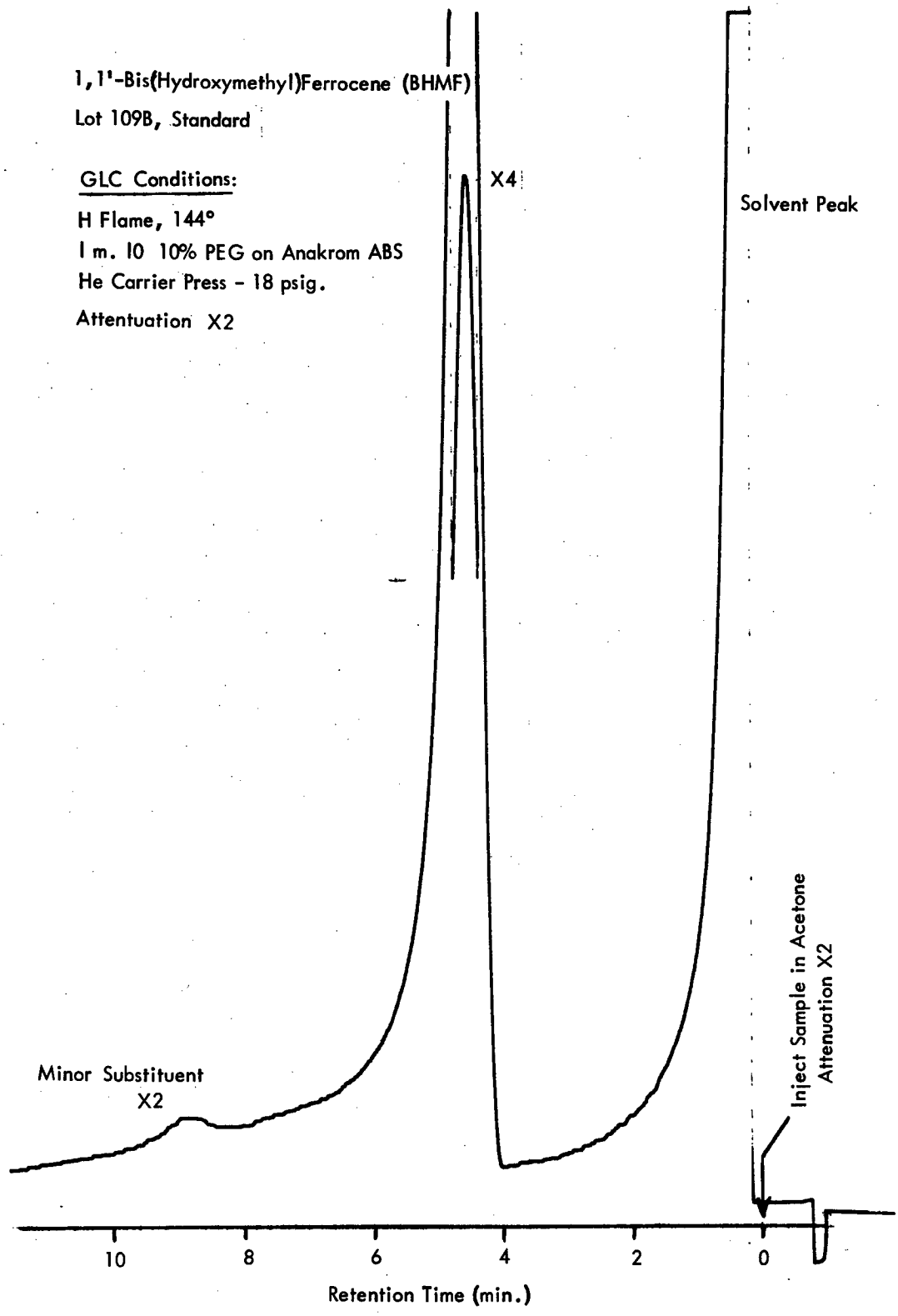


Figure 32 - Gas Liquid Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 109B, Standard)

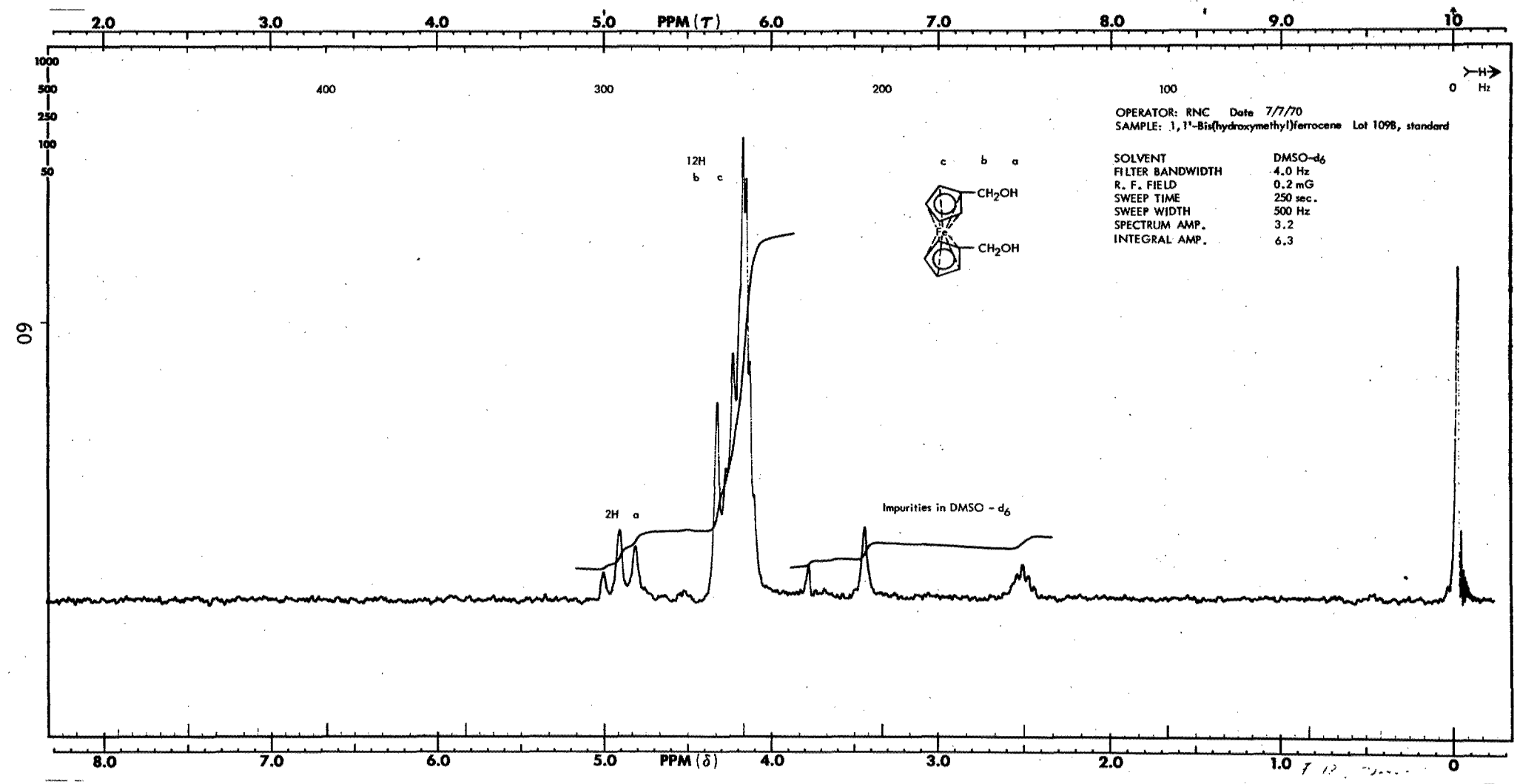


Figure 33 - NMR Spectrum of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 109B, Standard Lot)

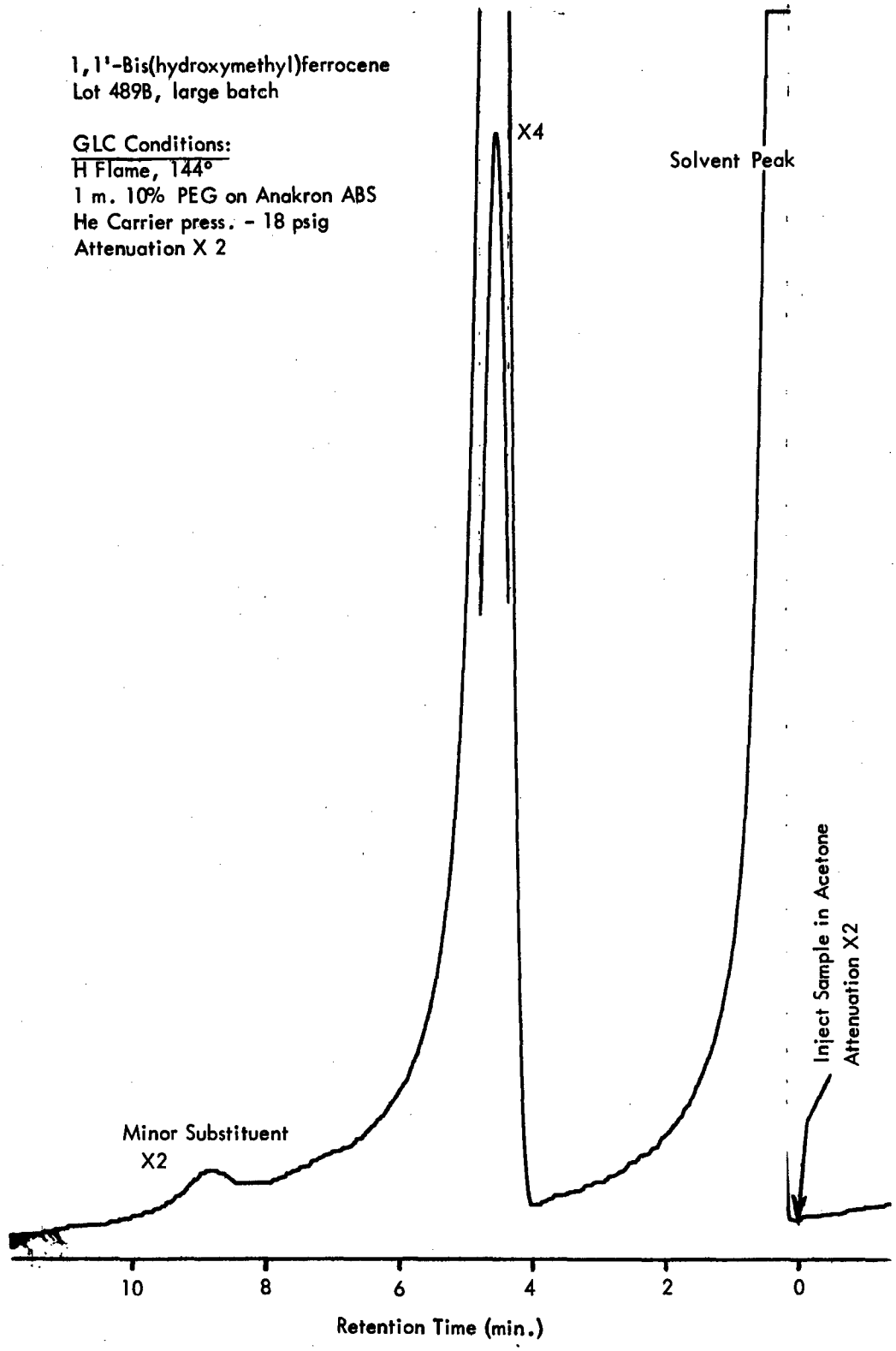


Figure 34 - Gas Liquid Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 489B)

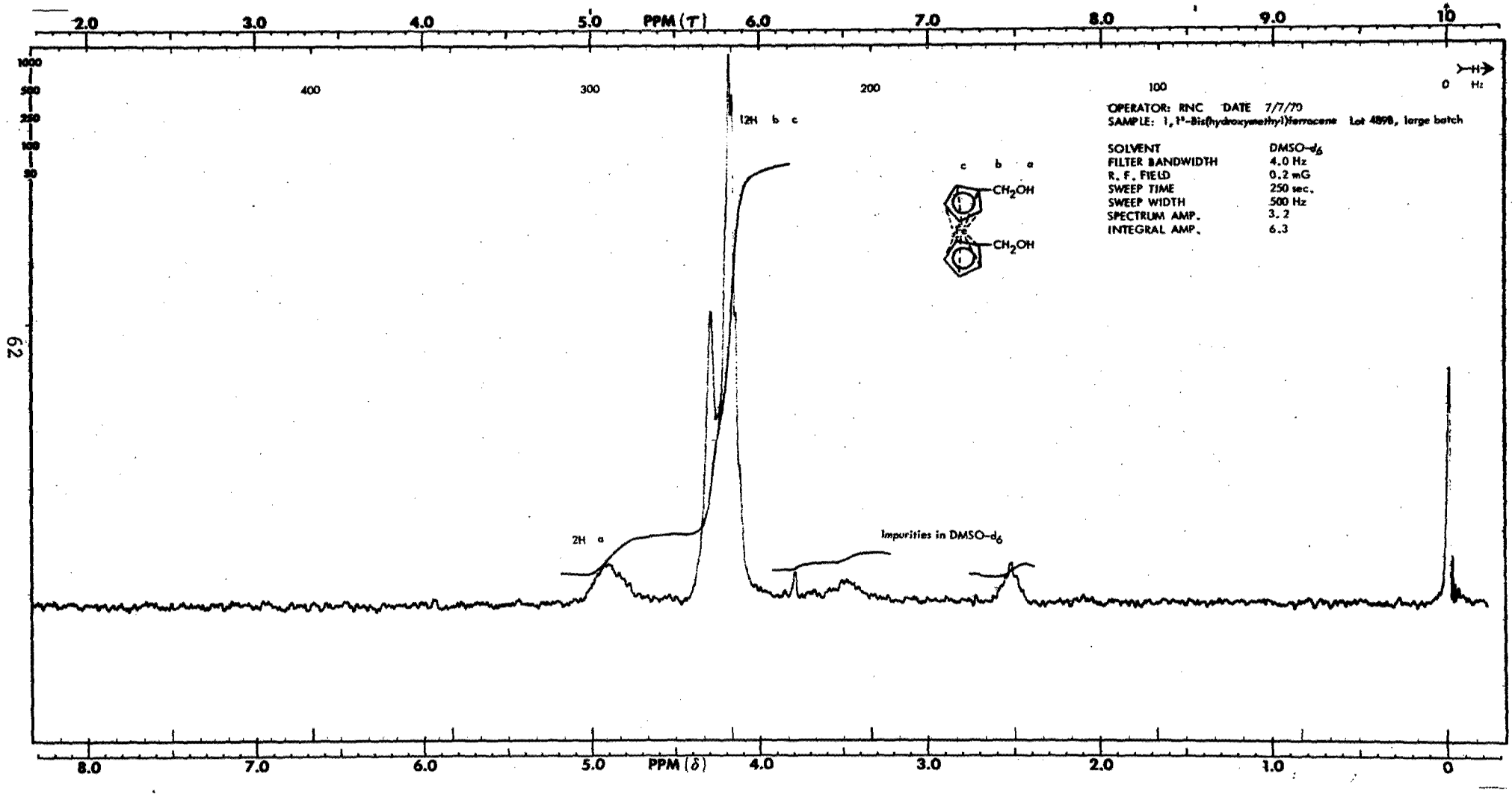


Figure 35 - NMR Spectrum of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 489B)

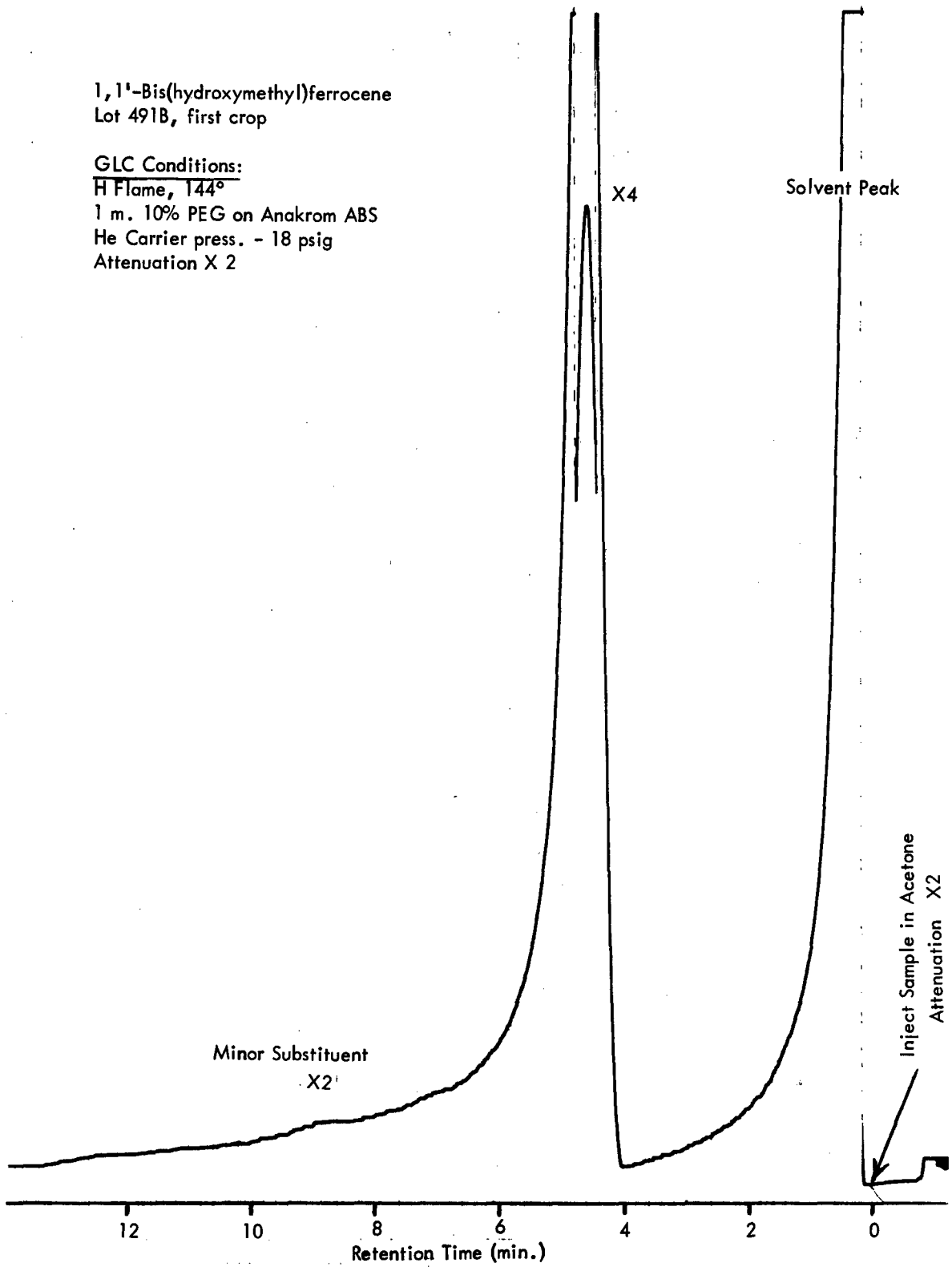


Figure 36 - Gas Liquid Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 491B, First Crop)

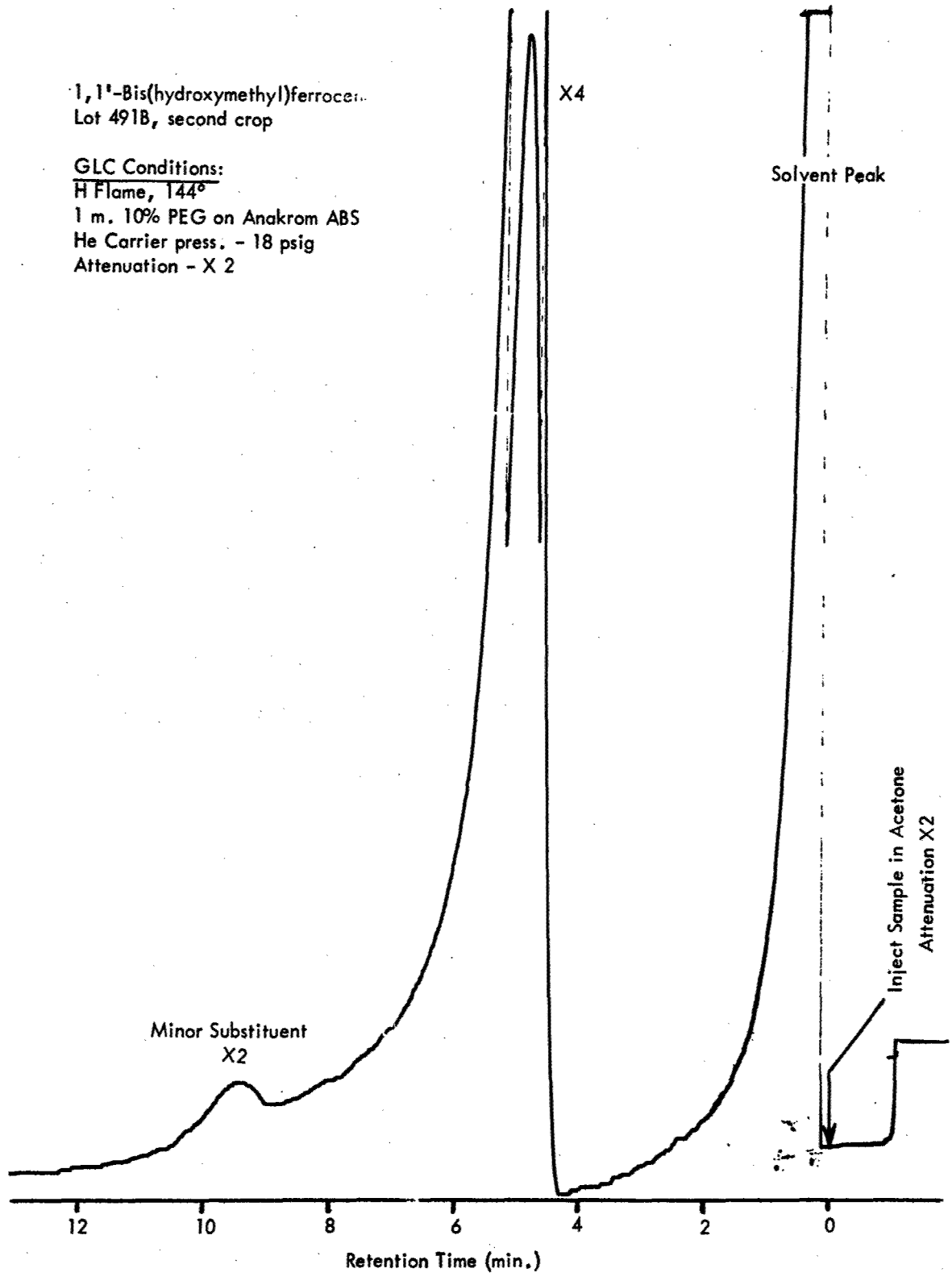


Figure 37 - Gas Liquid Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 491B, Second Crop)

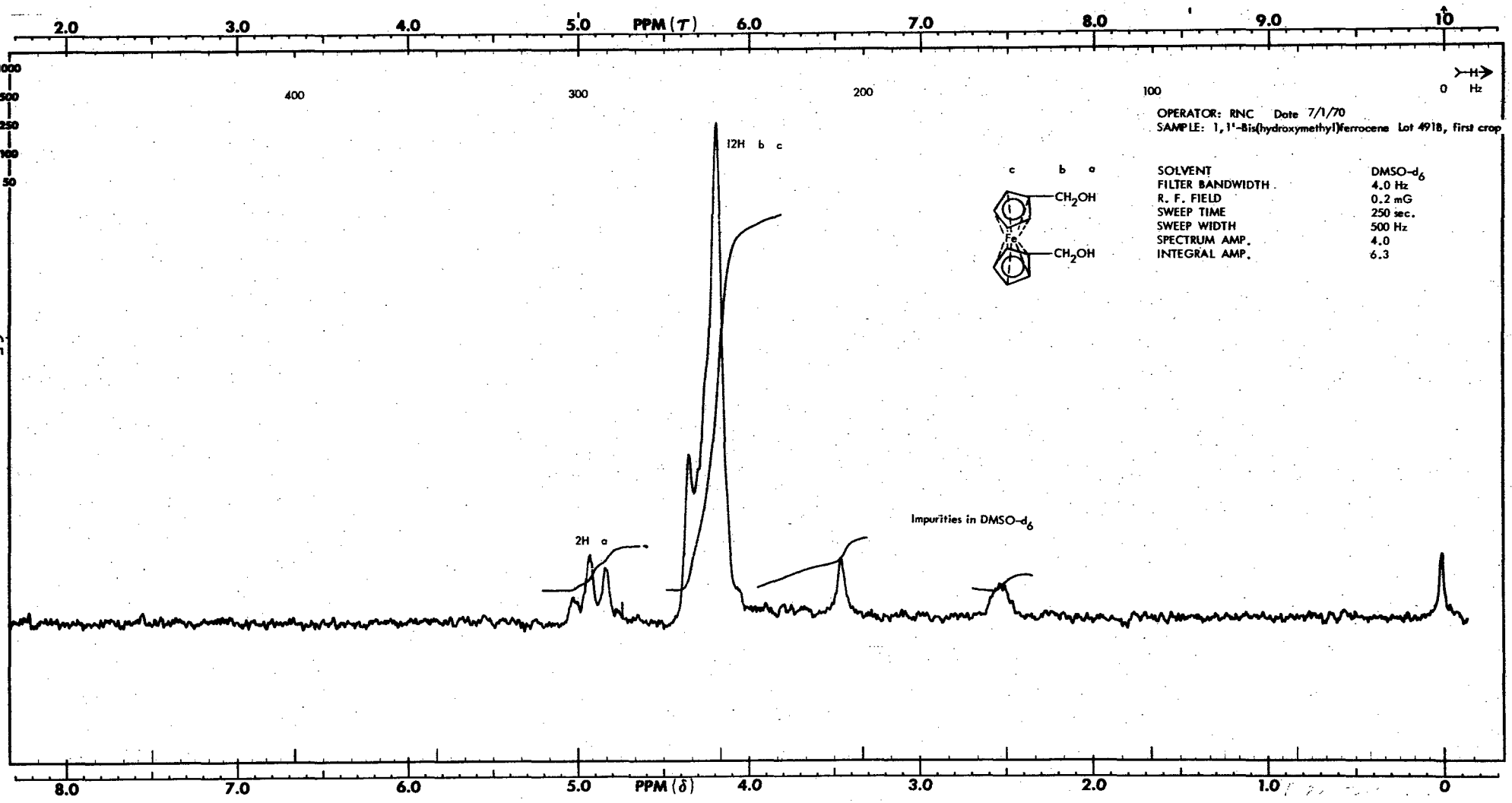


Figure 38 - NMR Spectrum of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 491B, First Crop)

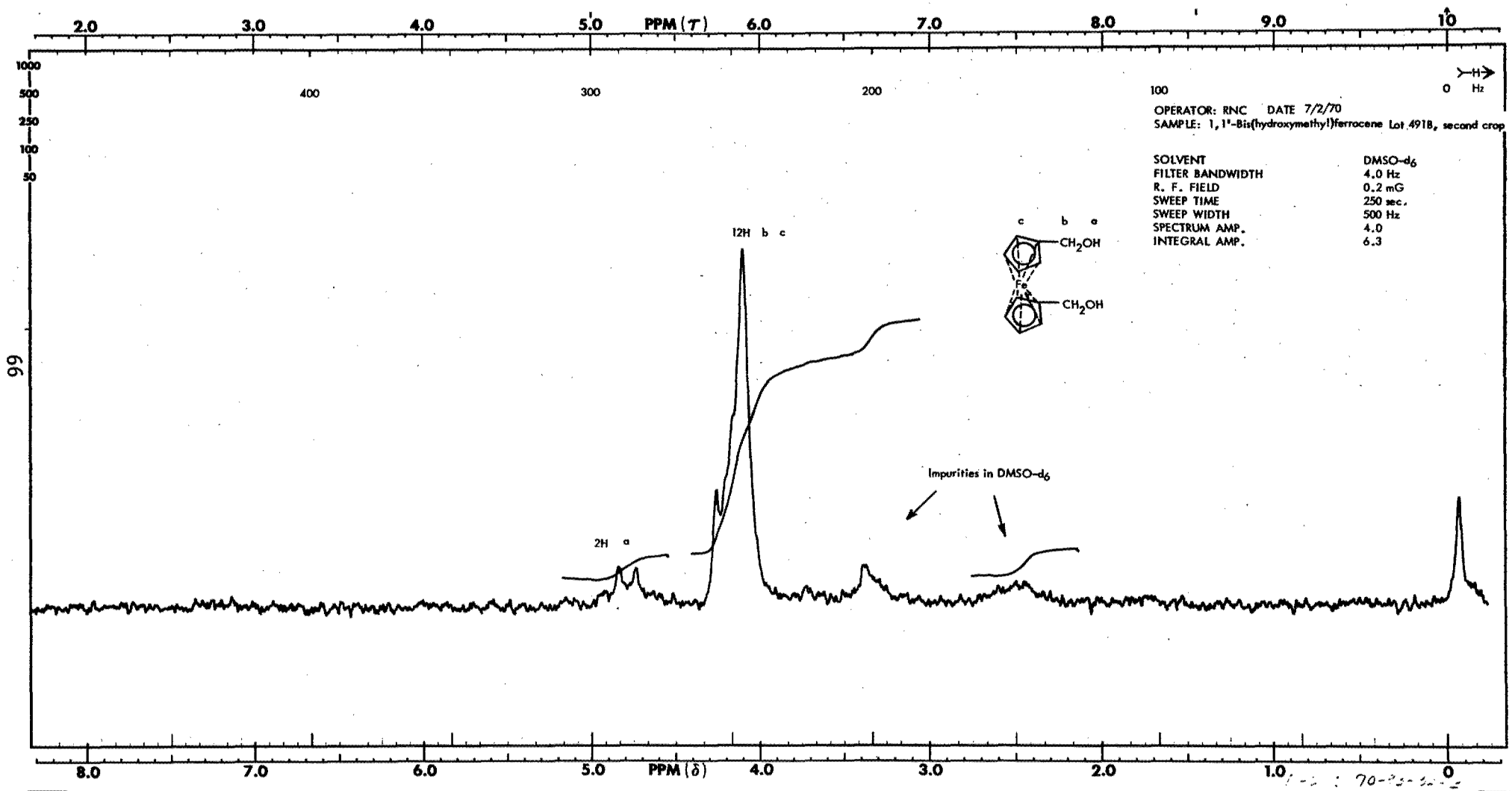


Figure 39 - NMR Spectrum of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 491B, Second Crop)

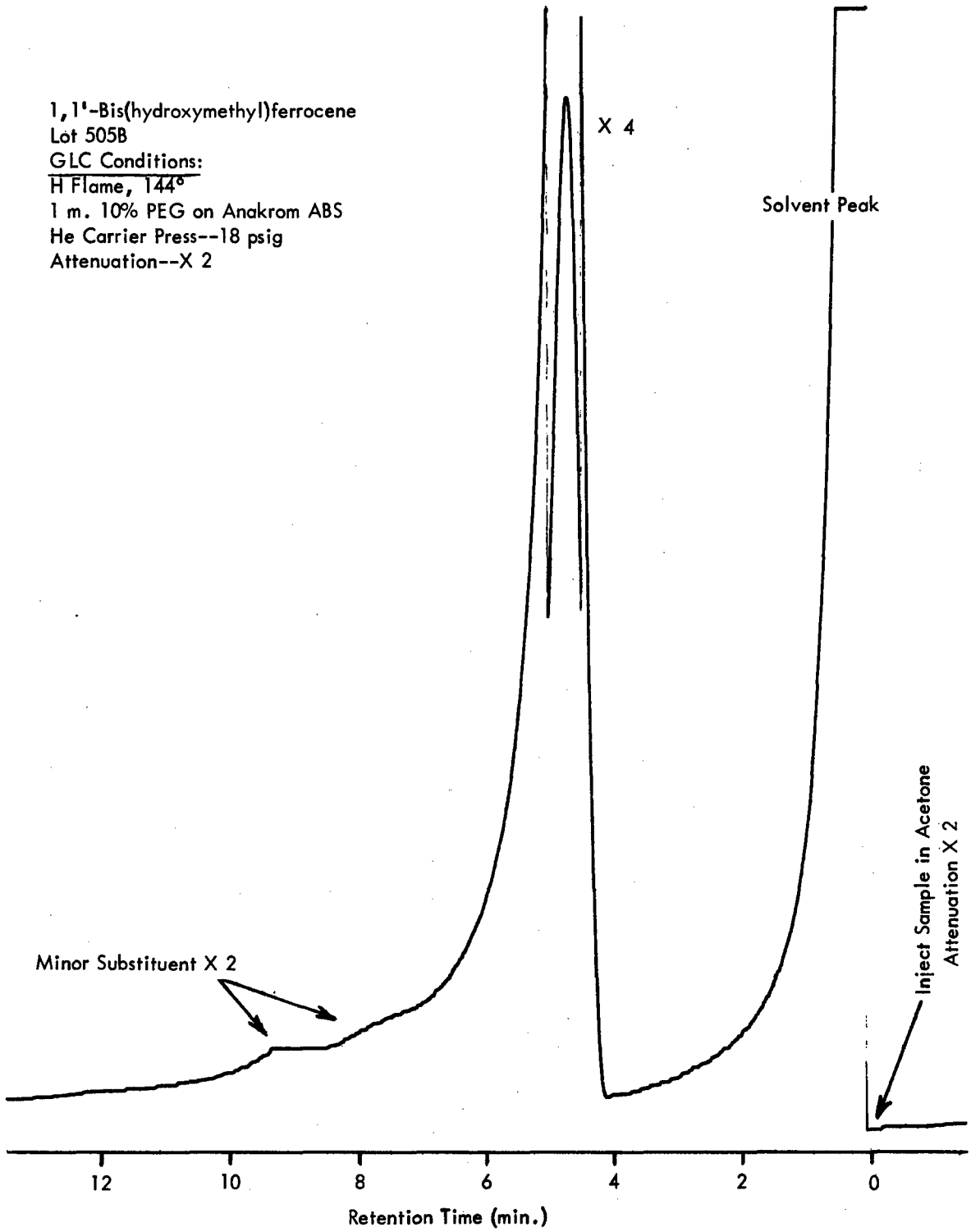


Figure 40 - Gas Liquid Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 505B)

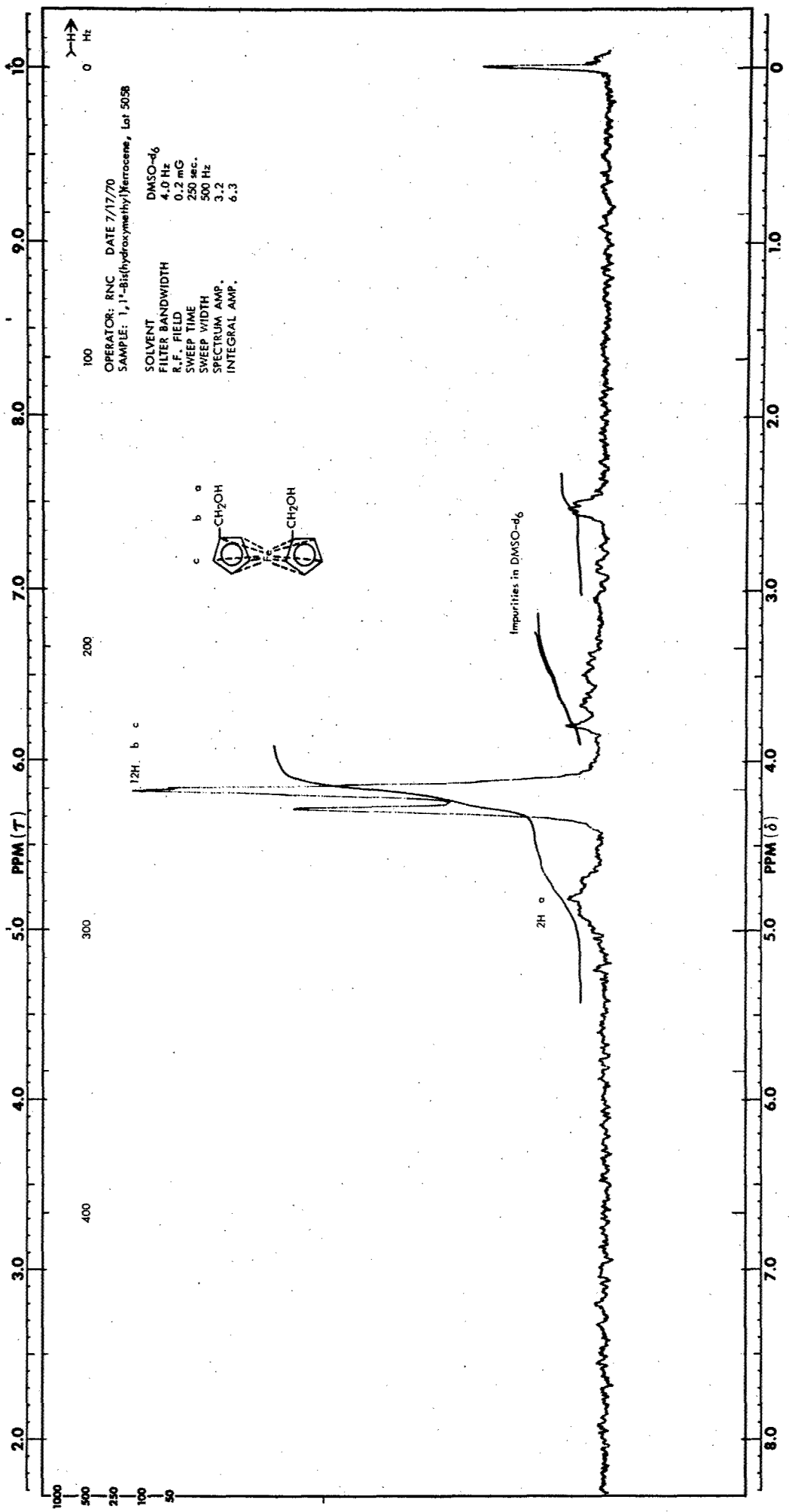


Figure 41 - NMR Spectrum of 1,1'-Bis(hydroxymethyl)ferrocene (Lot 505B)

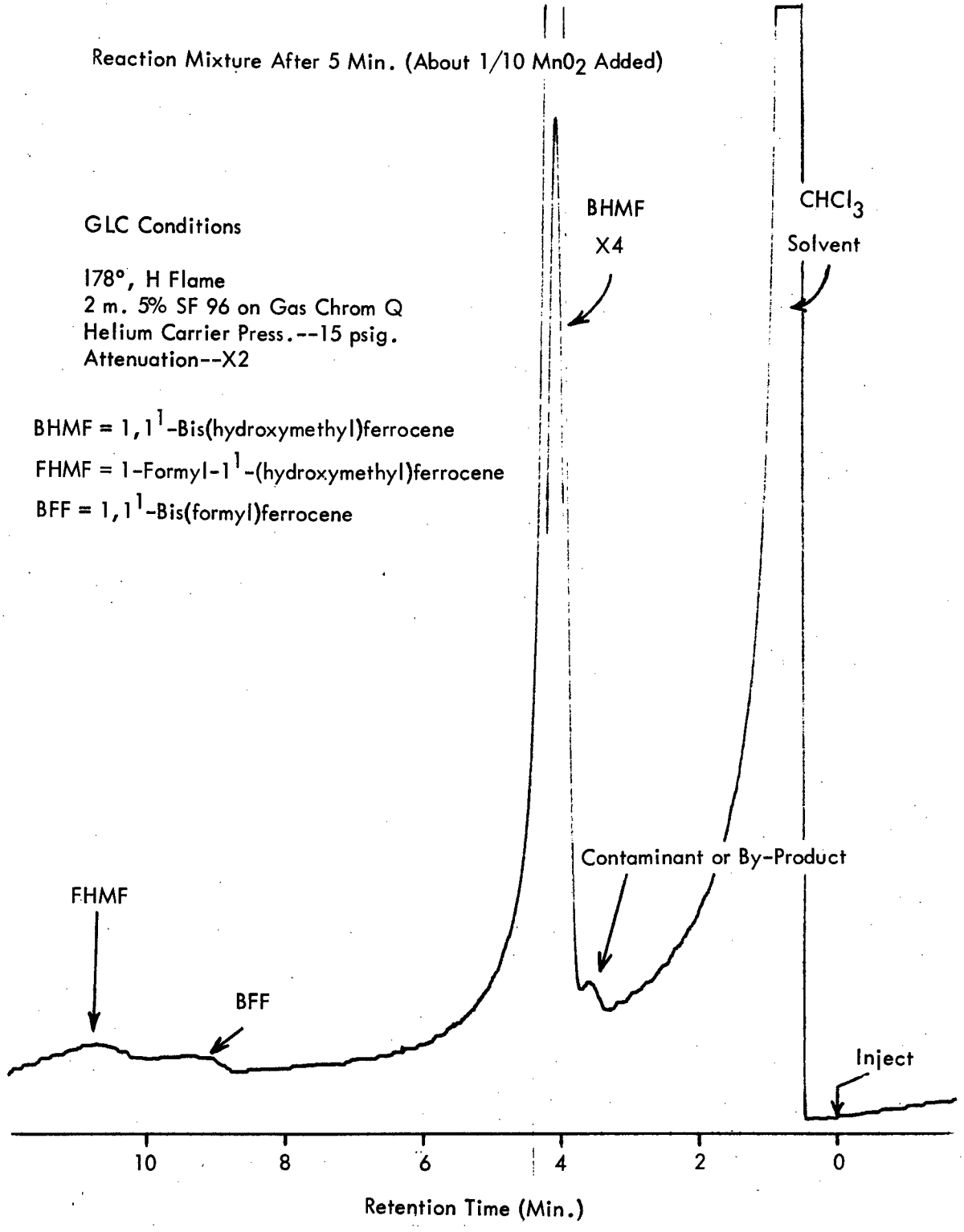


Figure 42 - GLC Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene Oxidation Mixture After 5 Min. (About 1/10 MnO_2 Added)

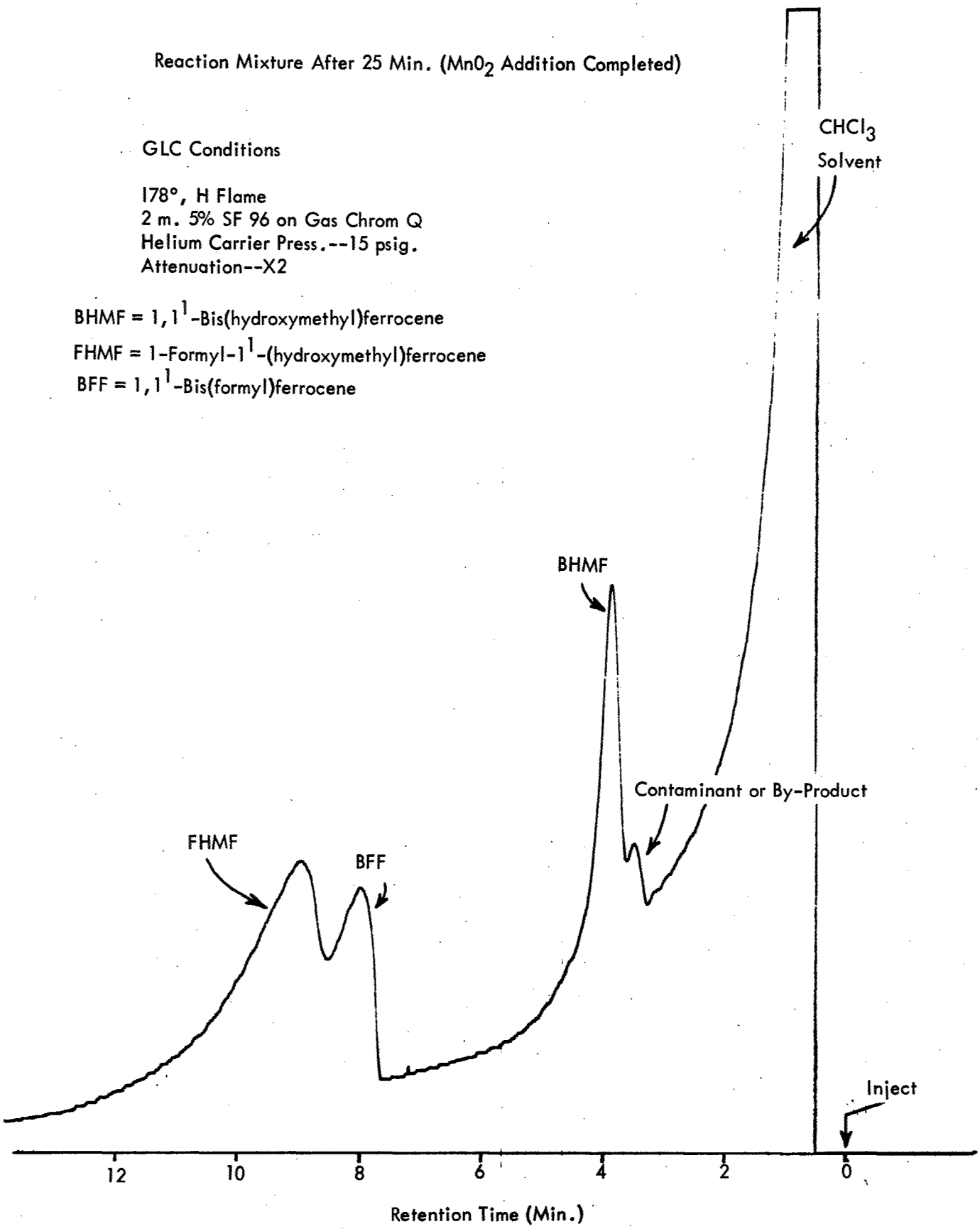


Figure 43 - GLC Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene Oxidation Mixture After 25 Min. (MnO_2 Addition Completed)

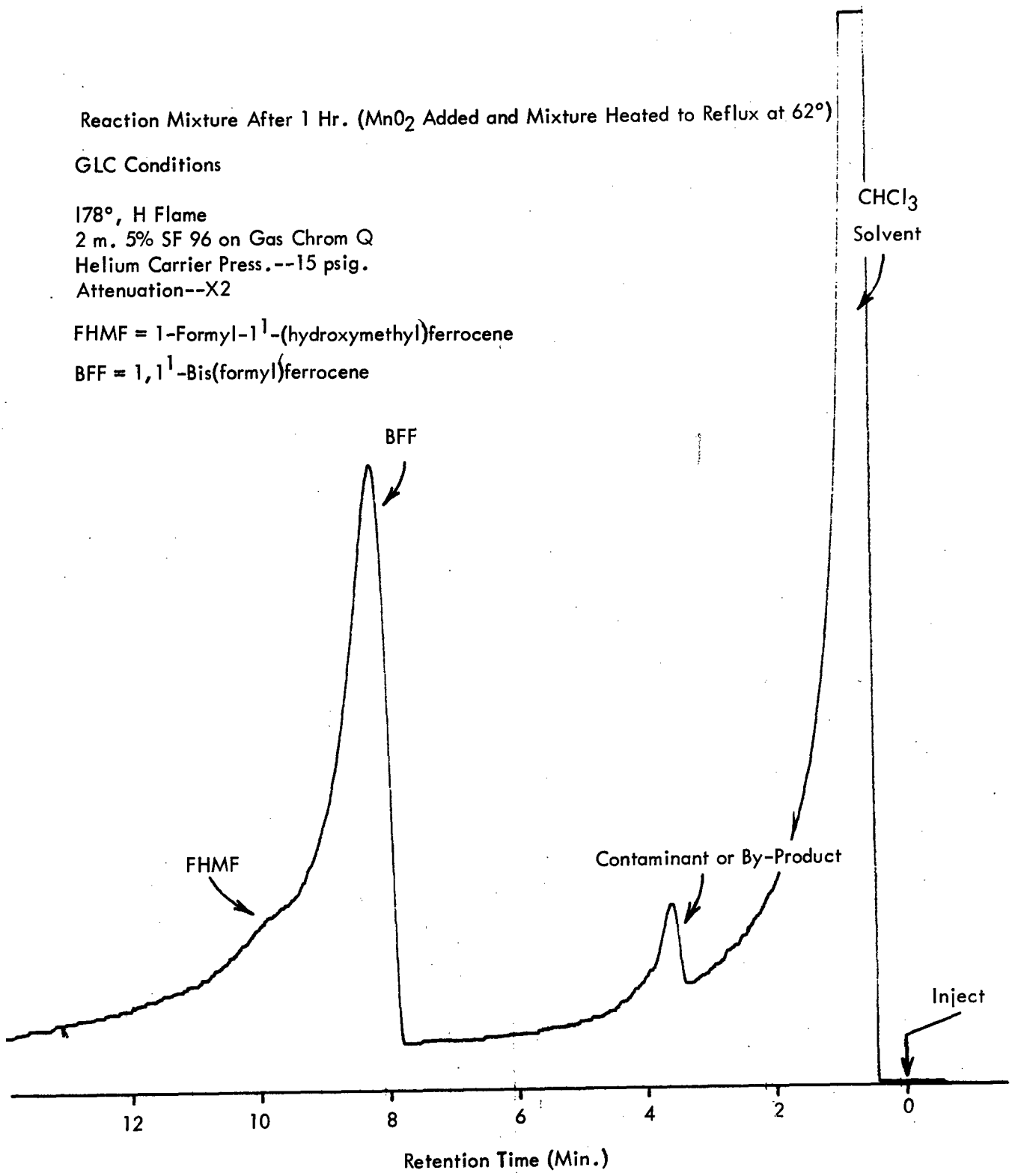


Figure 44 - GLC Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene Oxidation Mixture After 1 Hr. (MnO_2 Added and Mixture Heated to Reflux at 60°)

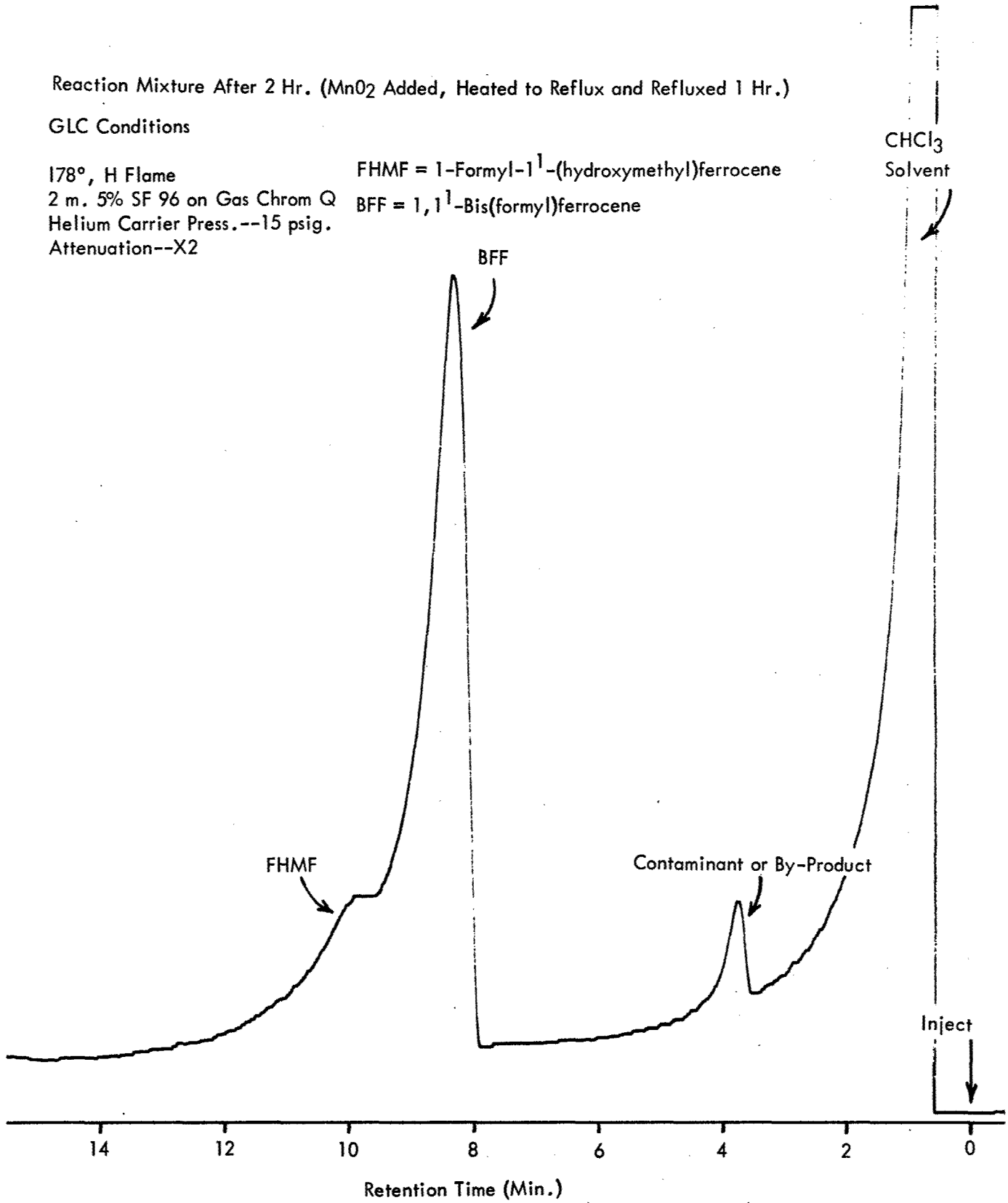


Figure 45 - GLC Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene Oxidation Mixture After 2 Hr. (MnO_2 Added, Heated to Reflux and Refluxed 1 Hr.)

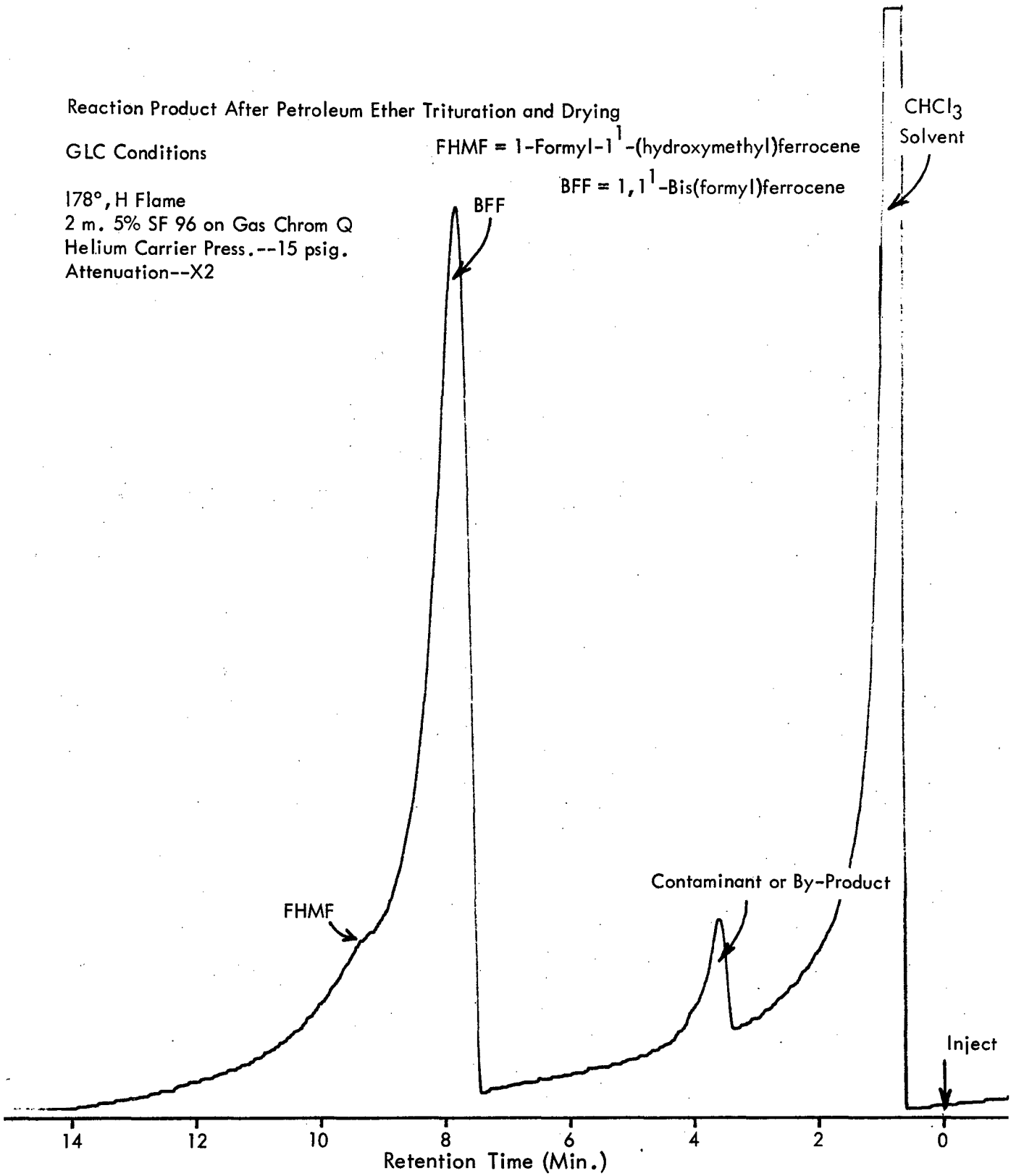


Figure 46 - GLC Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene Oxidation Product After Petroleum Ether Trituration and Drying

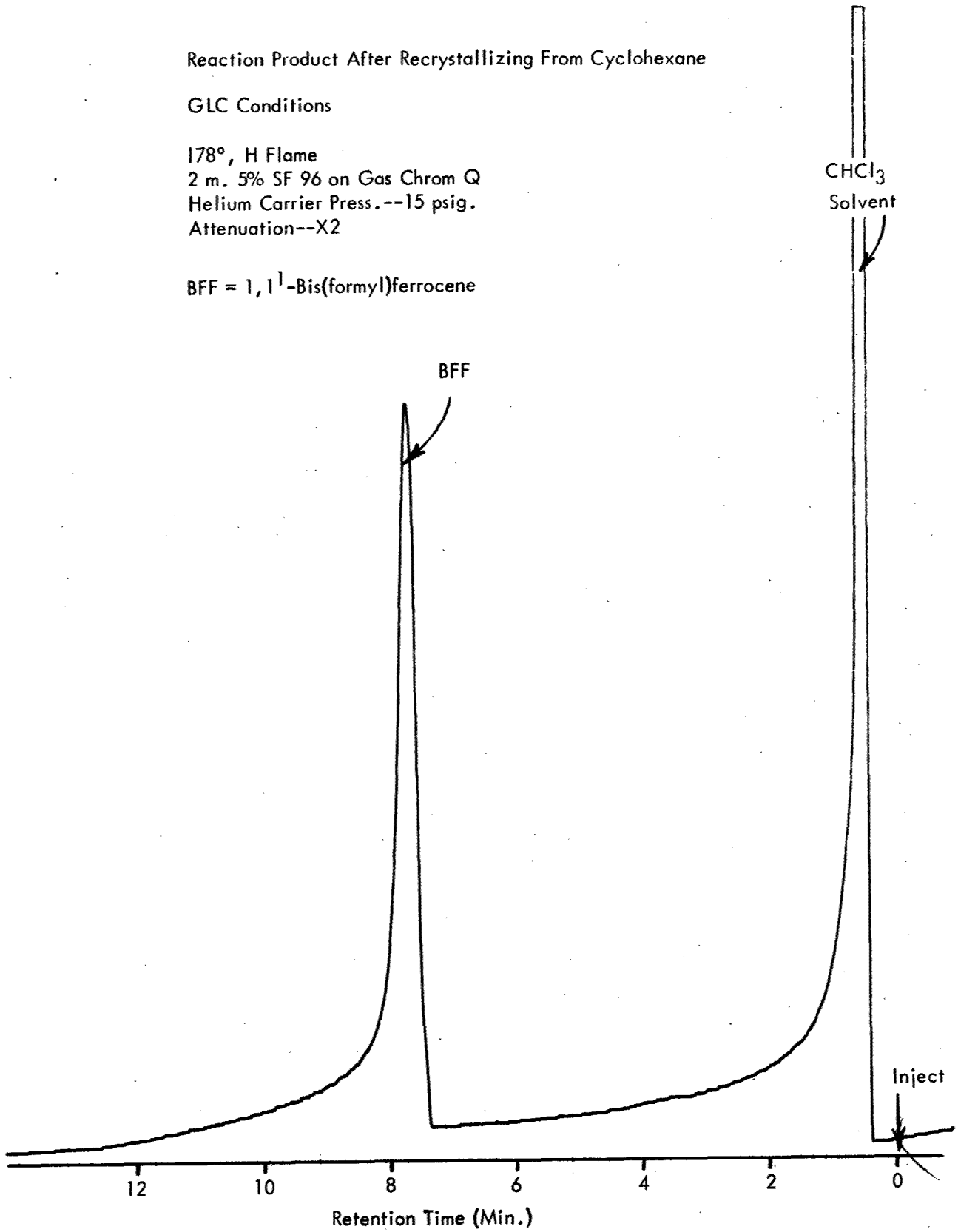


Figure 47 - GLC Chromatogram of 1,1'-Bis(hydroxymethyl)ferrocene Oxidation Product After Recrystallizing from Cyclohexane

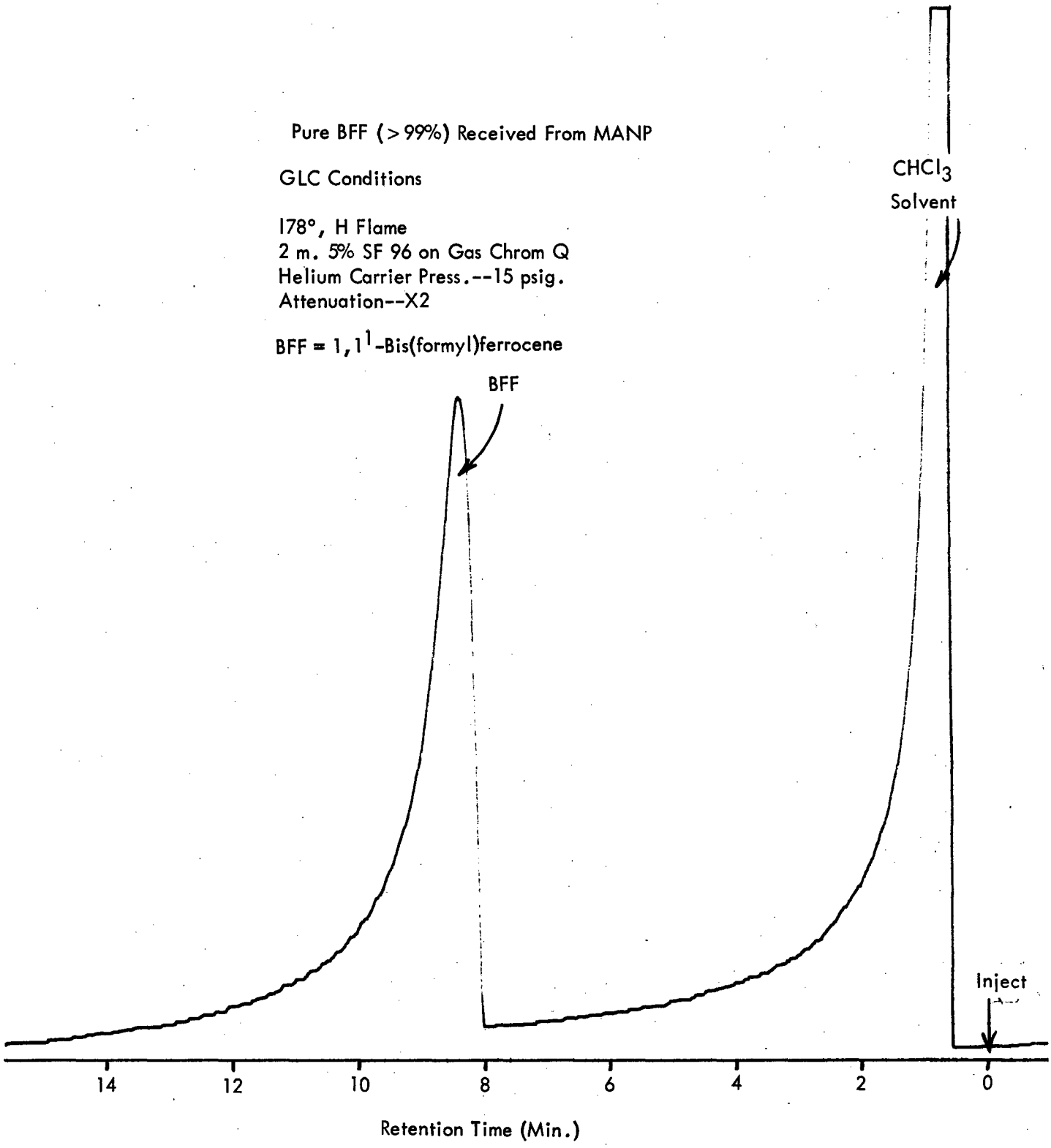


Figure 48 - GLC Chromatogram of 1,1'-Bis(formyl)ferrocene (99% Pure Received from LNP)

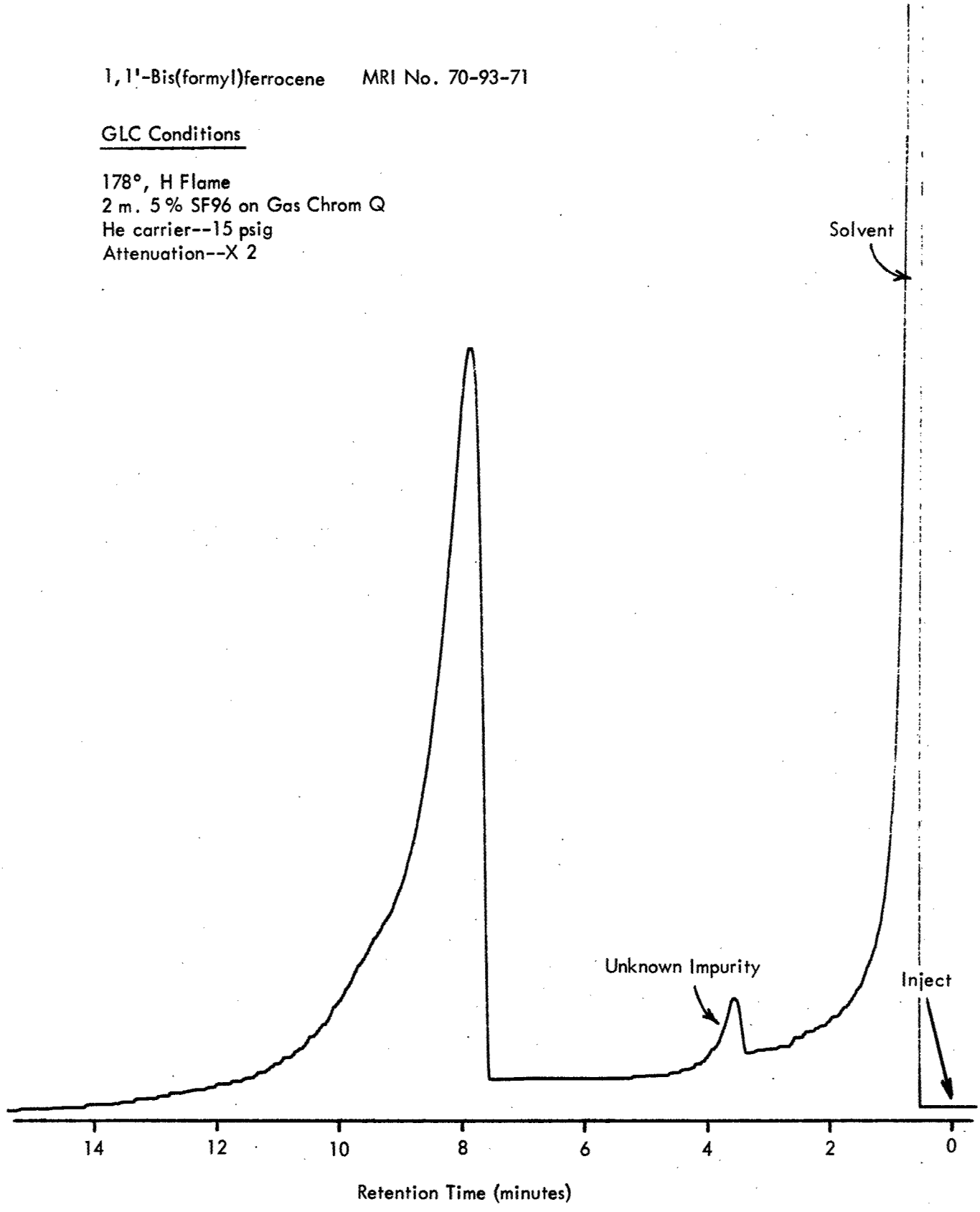


Figure 49 - GLC Chromatogram of 1,1'-Bis(formyl)ferrocene (Sample No. 1)

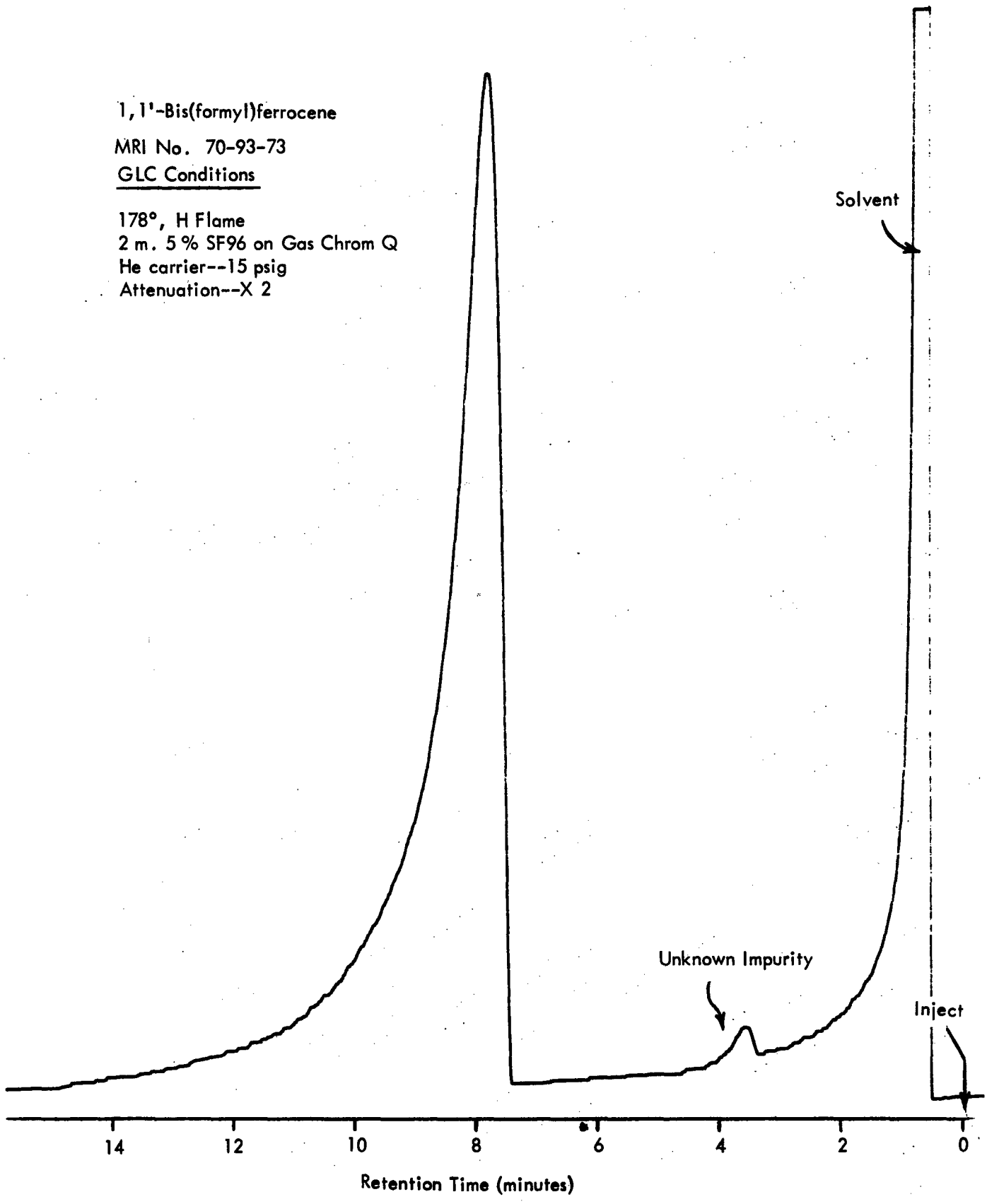


Figure 50 - GLC Chromatogram of 1,1'-Bis(formyl)ferrocene (Sample No. 2)

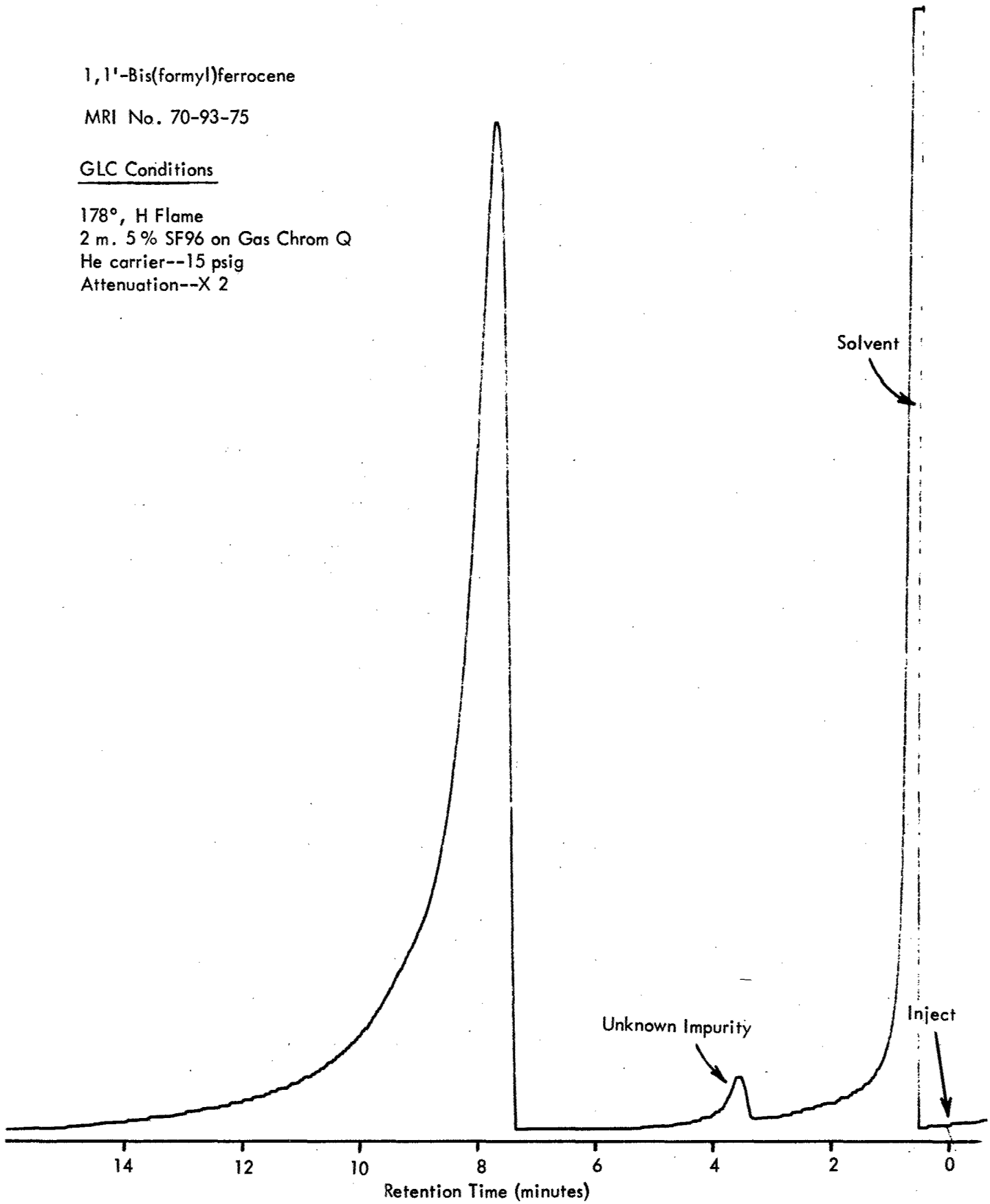


Figure 51 - GLC Chromatogram of 1,1'-Bis(formyl)ferrocene (Sample No. 3)

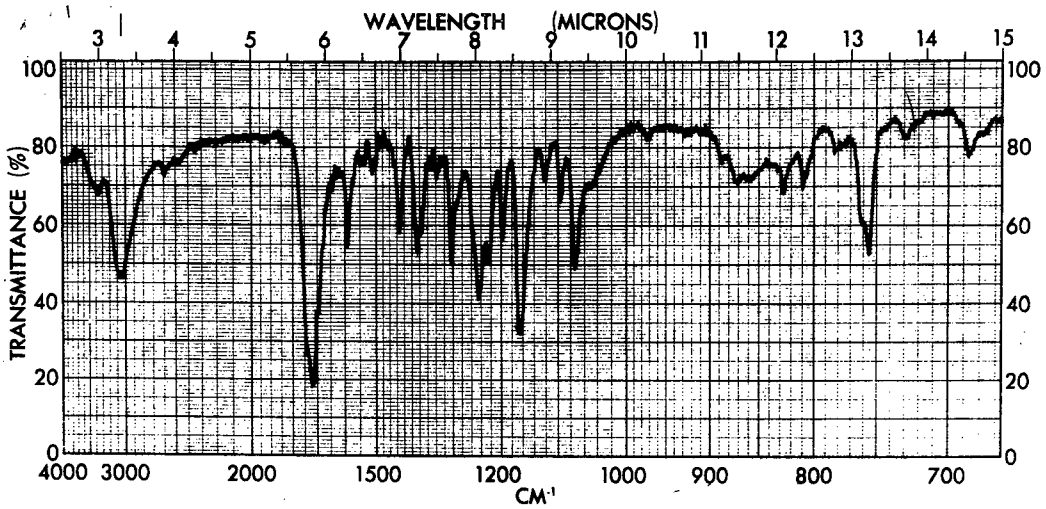


Figure 52 - Infrared Spectrum of NTCA No. 1 (Beaufort Chemical Company) (KBr)

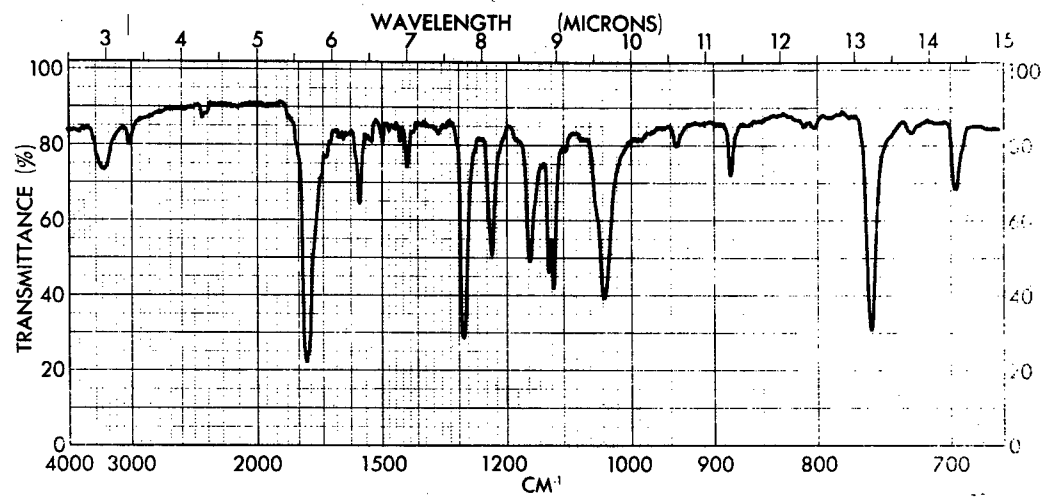


Figure 53 - Infrared Spectrum of NTCA Dianhydride (Produced by Heating NTCA No. 1 on DTA to 300°C) (KBr)

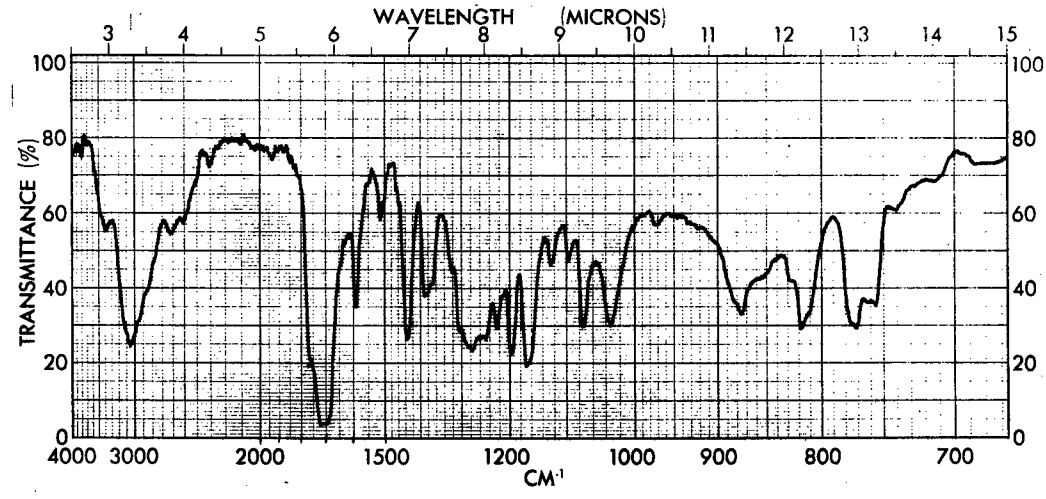


Figure 54 - Infrared Spectrum of NTCA No. 2 (Celanese via LNP 23 September 1969) (KBr)

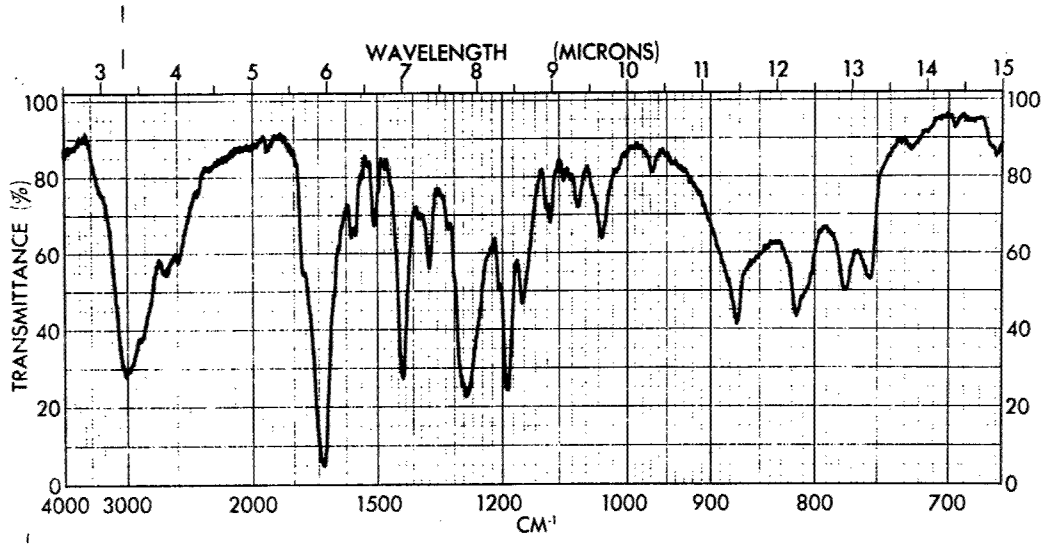


Figure 55 - Infrared Spectrum of NTCA No. 3 (Celanese via LNP 14 October 1970) (KBr)

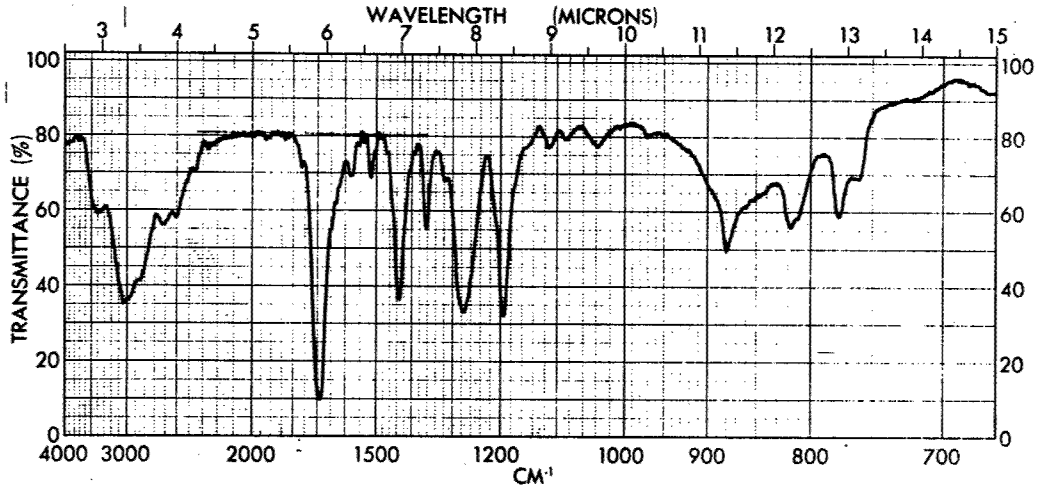


Figure 56 - Infrared Spectrum of NTCA No. 4 (Used in Polymerization 69-1) (KBr)

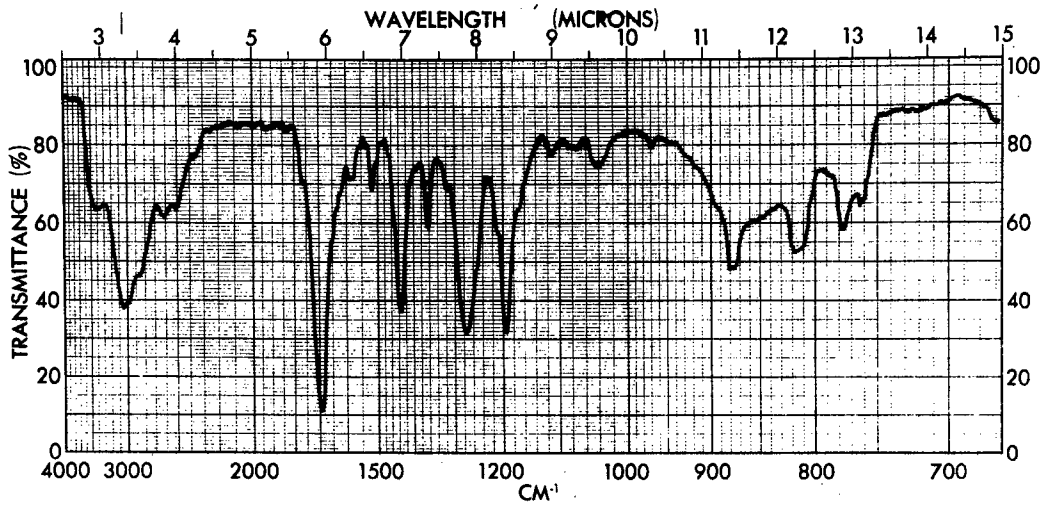


Figure 57 - Infrared Spectrum of NTCA No. 5 (Used in Polymerization 70-1) (KBr)

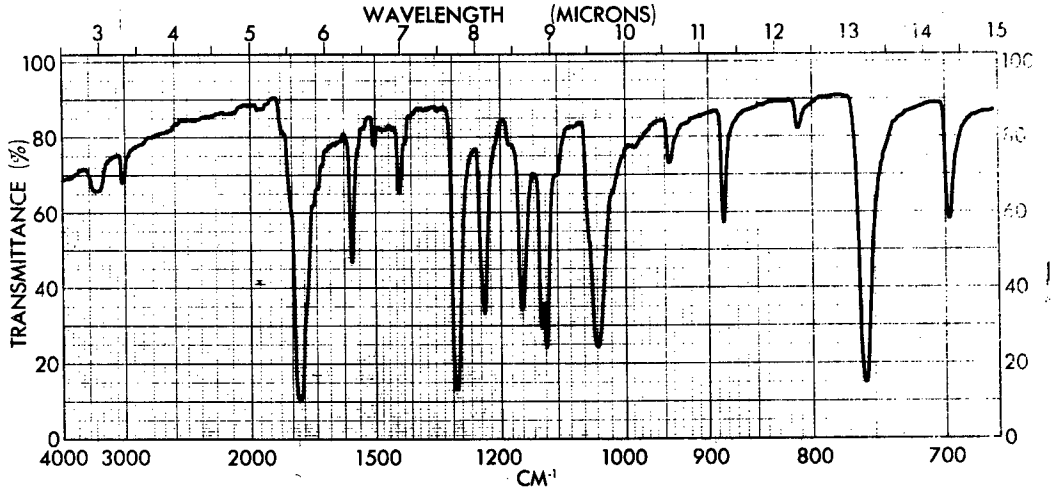


Figure 58 - Infrared Spectrum of NTCA Dianhydride (Produced by Heating NTCA No. 5 on DTA to 350°) (KBr)

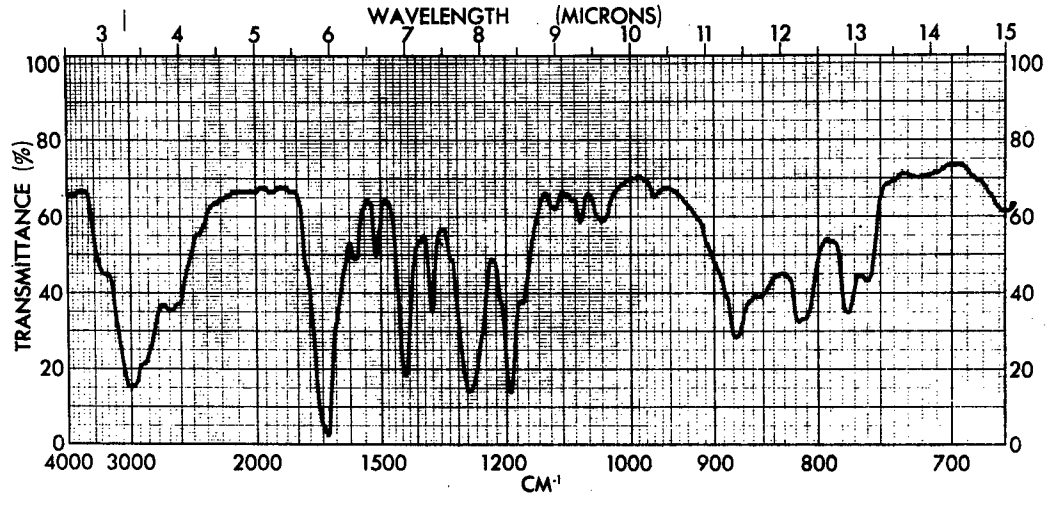


Figure 59 - Infrared Spectrum of NTCA (Produced by Three Successive Oxidation-Decolorization Treatments of the NTCA No. 1) (KBr)

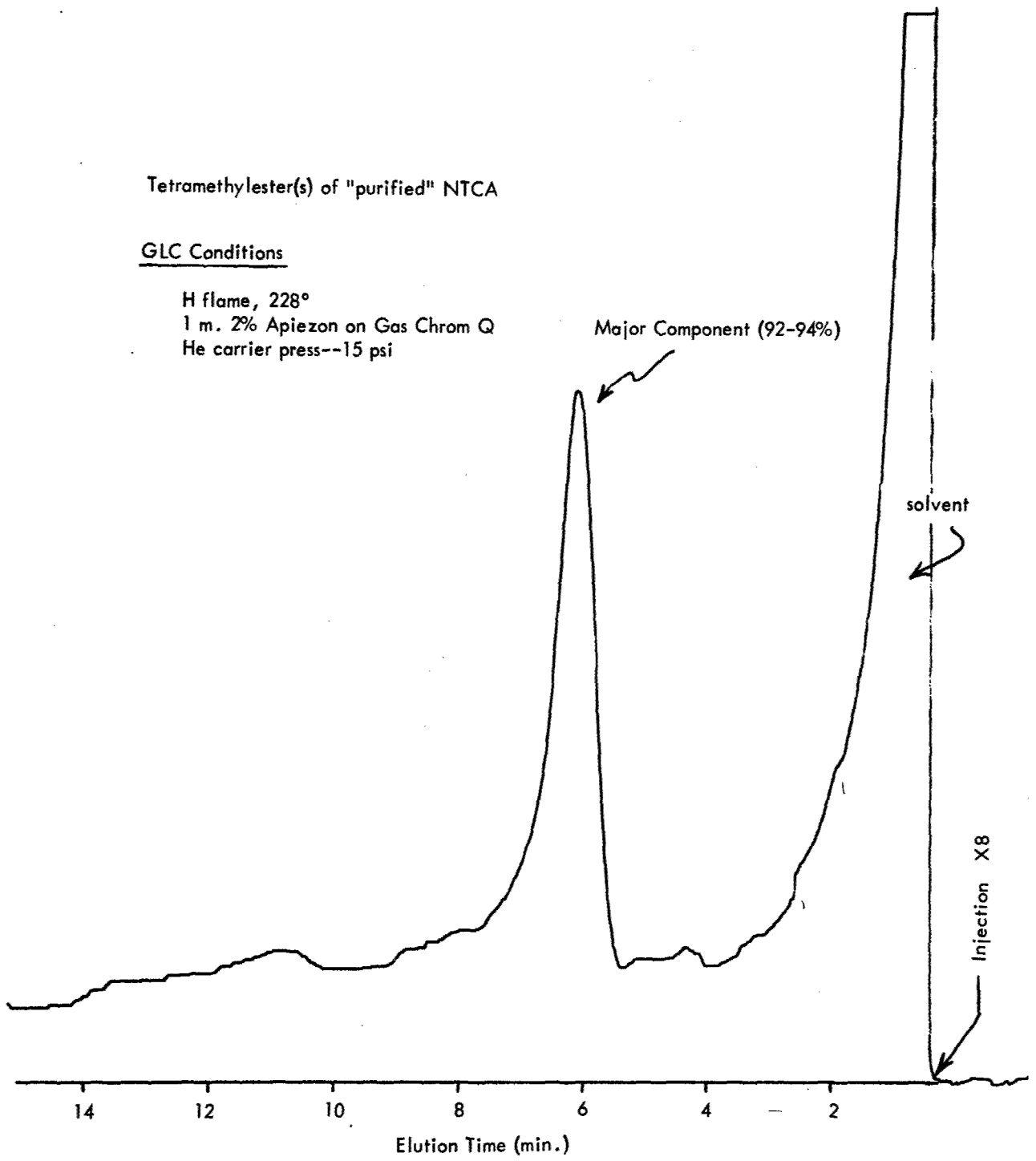


Figure 60 - Gas Liquid Chromatogram of Tetramethyl Ester(s) of NTCA No. 5

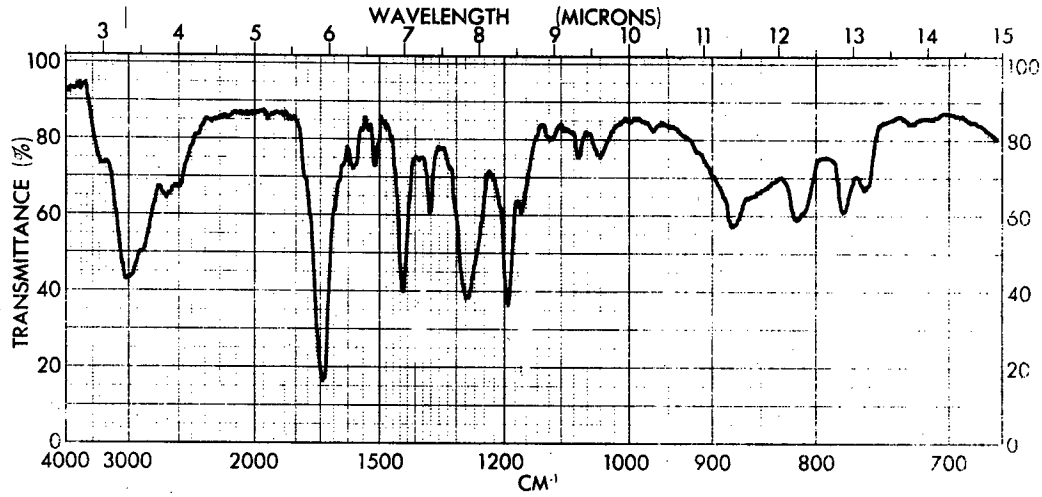


Figure 61 - Infrared Spectrum of NTCA No. 6 (1 g. of NTCA No. 5 Treated 15 Min. with 100 Ml. 12N HCl) (KBr)

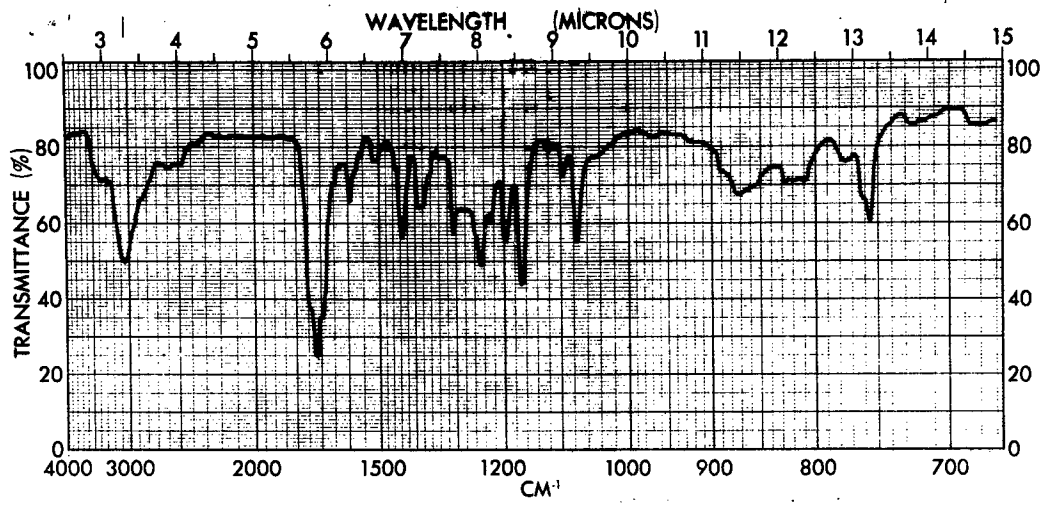


Figure 62 - Infrared Spectrum of NTCA No. 7 (5 g. of NTCA No. 5 Treated 20 Hr. with 6N HCl) (Used in Polymerization 70-2) (KBr)

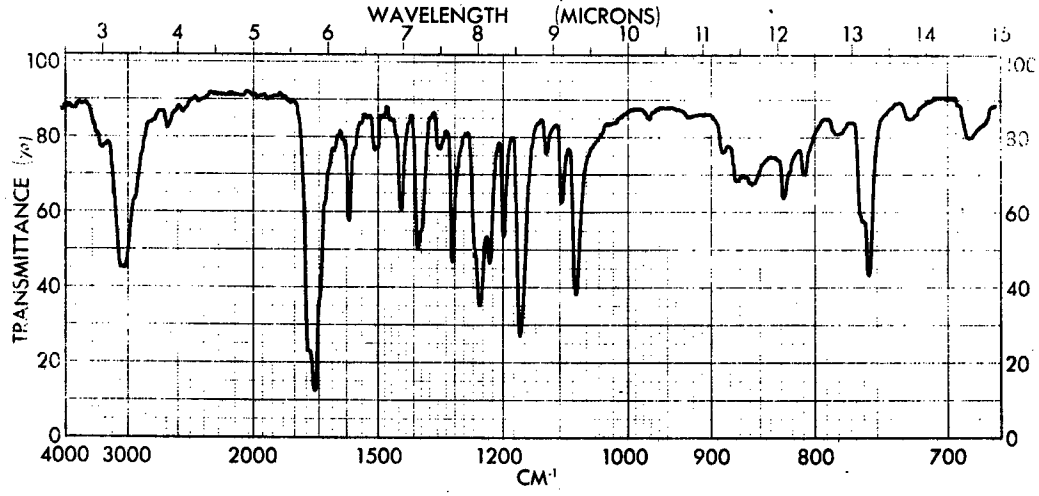


Figure 63 - Infrared Spectrum of NTCA No. 8 (5 g. of NTCA No. 5 After 66 Hr. Treatment with 6N HCl) (Used in Polymerization 70-3) (KBr)

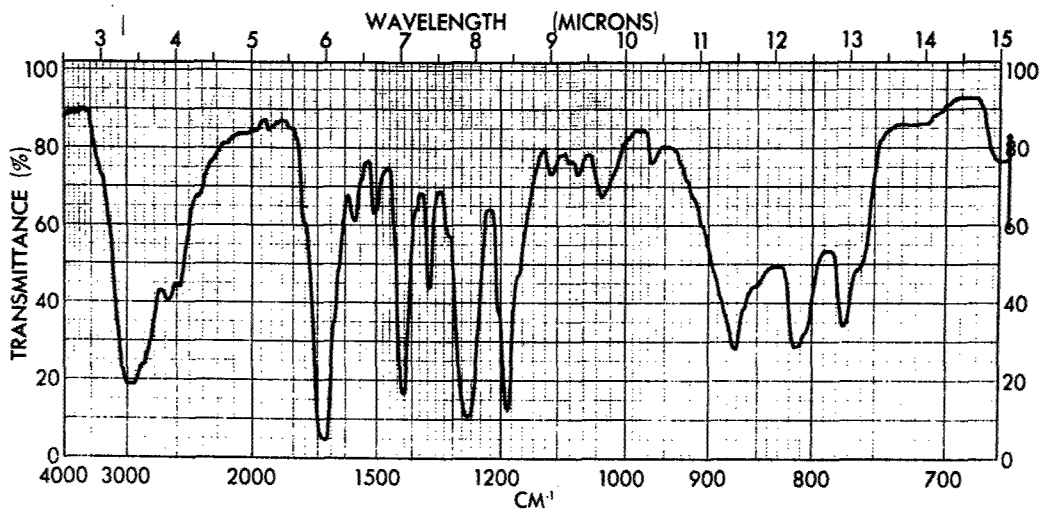


Figure 64 - Infrared Spectrum of NTCA No. 9 (Used in Polymerization 70-4) (KBr)

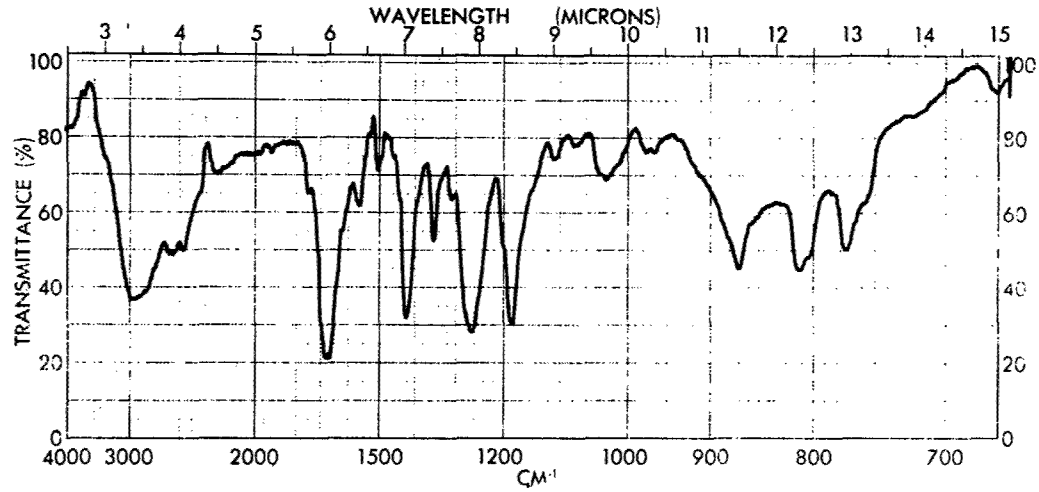


Figure 65 - Infrared Spectrum of NTCA No. 10 (Used in Polymerization 70-5) (KBr)

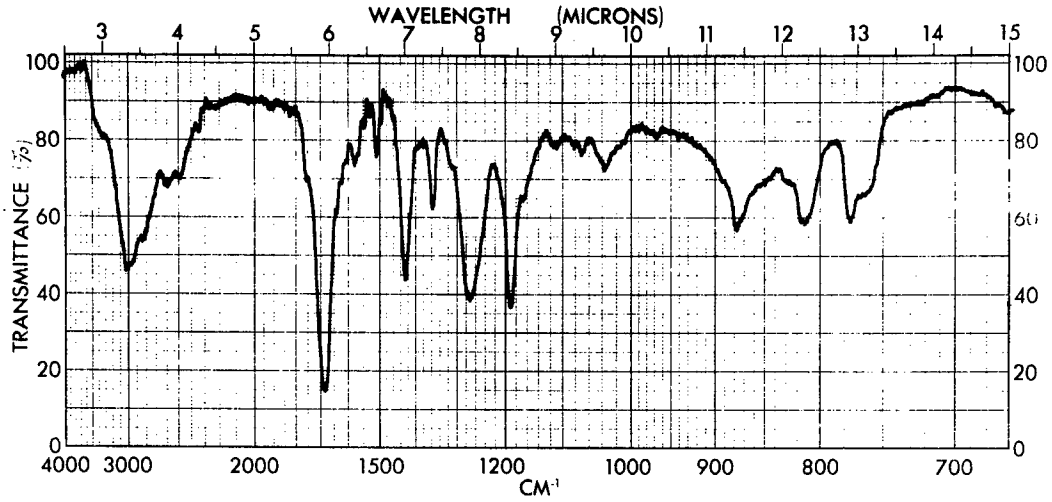


Figure 66 - Infrared Spectrum of NTCA No. 11 (Used in Polymerization No. 70-6) (KBr)

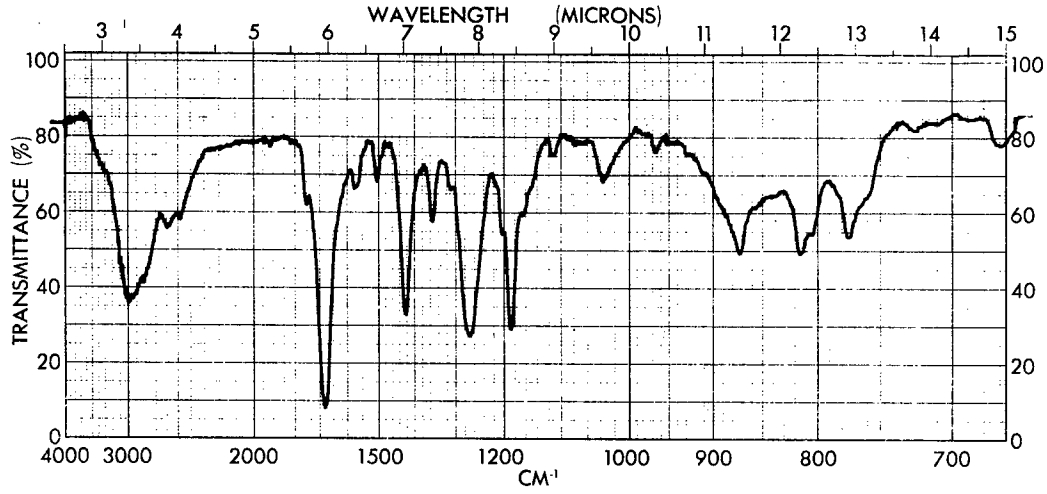


Figure 67 - Infrared Spectrum of NTCA No. 12 (Used in Polymerization No. 70-7) (KBr)

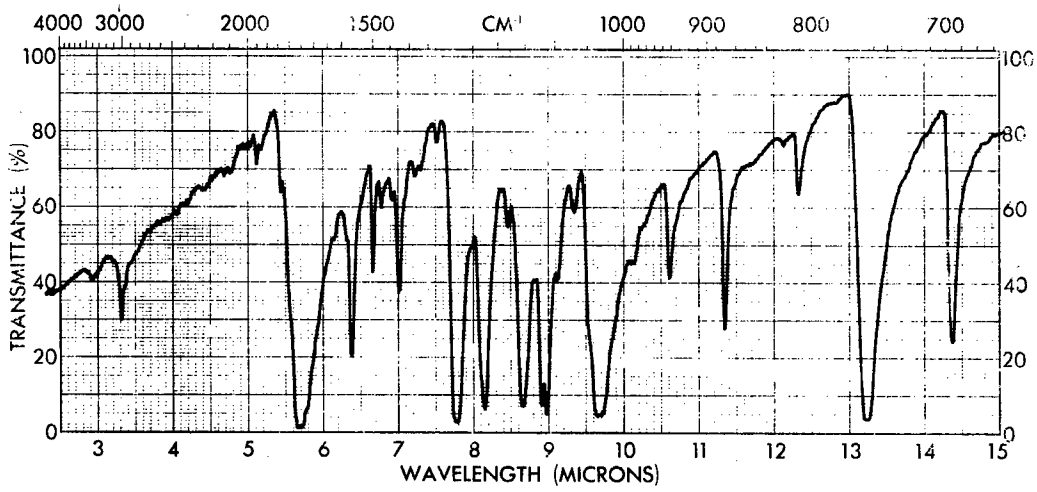


Figure 68 - Infrared Spectrum of Commercial NTDA (Source: Aldrich Chemical Company) (KBr)

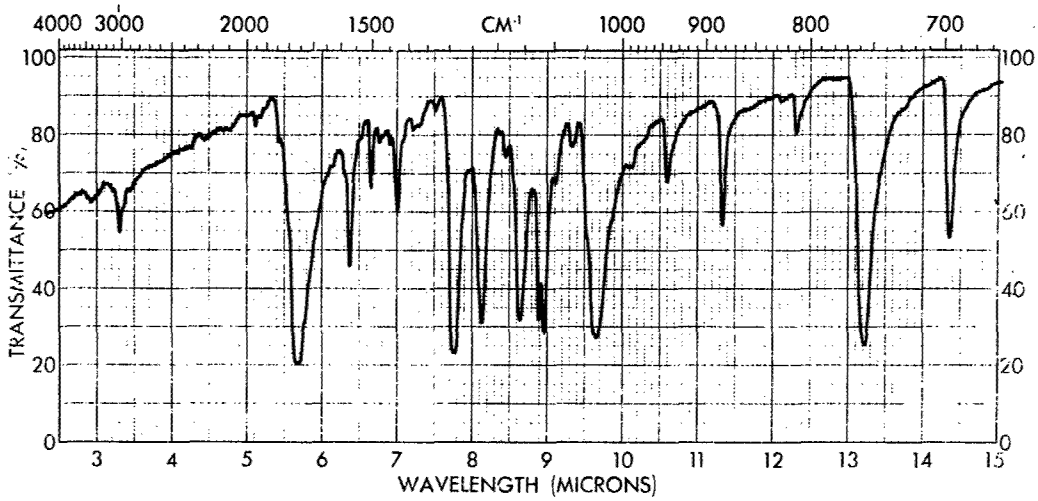


Figure 69 - Infrared Spectrum of Commercial NTDA (Source: Chemical Procurement Labs) (KBr)

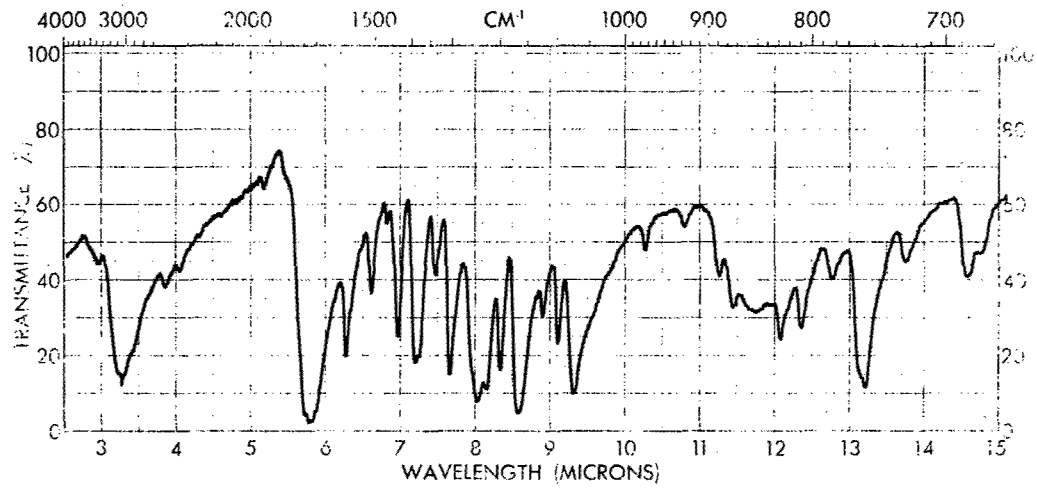


Figure 70 - Infrared Spectrum of Commercial NTDA (Source: K and K Laboratories) (KBr)

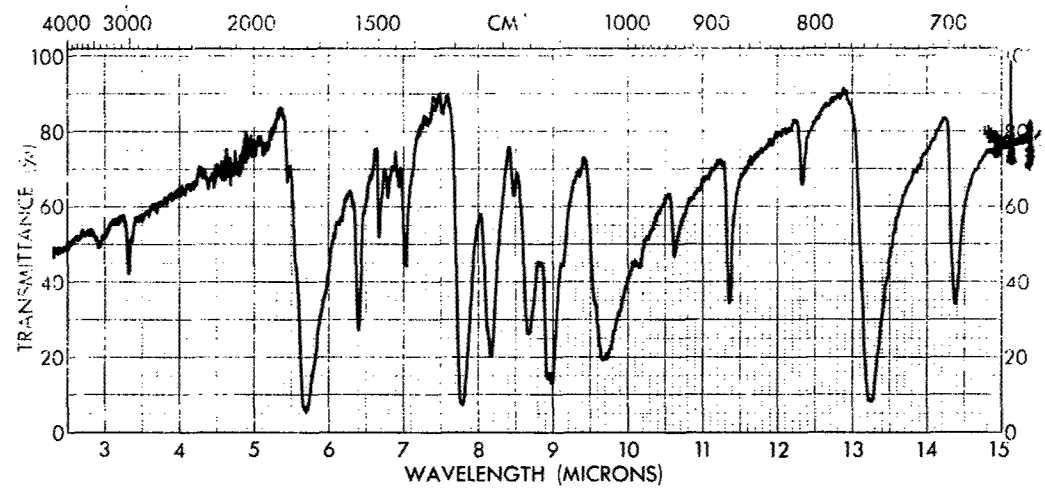


Figure 71 - Infrared Spectrum of NTDA No. 1 (Used in Polymerization No. 71-1) (KBr)

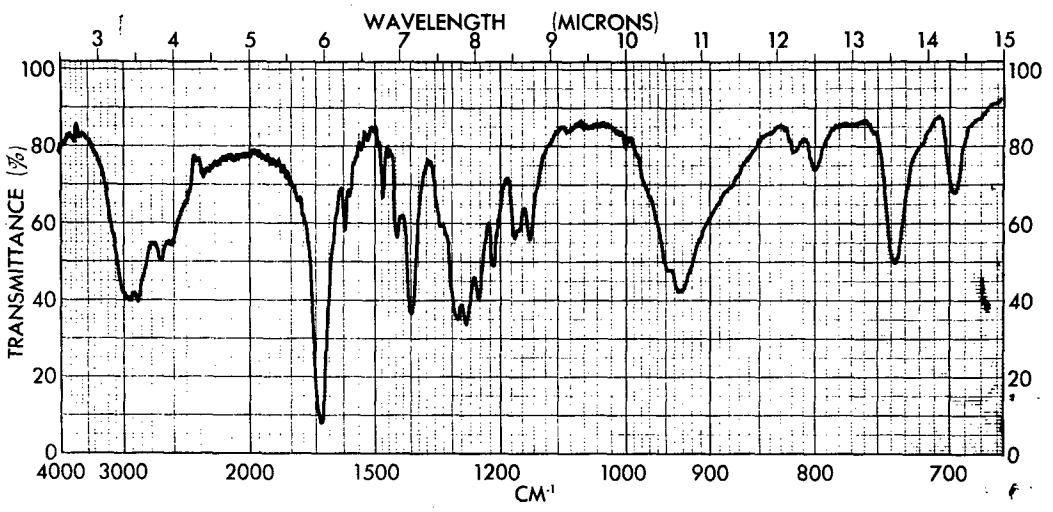


Figure 72 - Infrared Spectrum of m-Pheylenediacetic Acid (KBr)

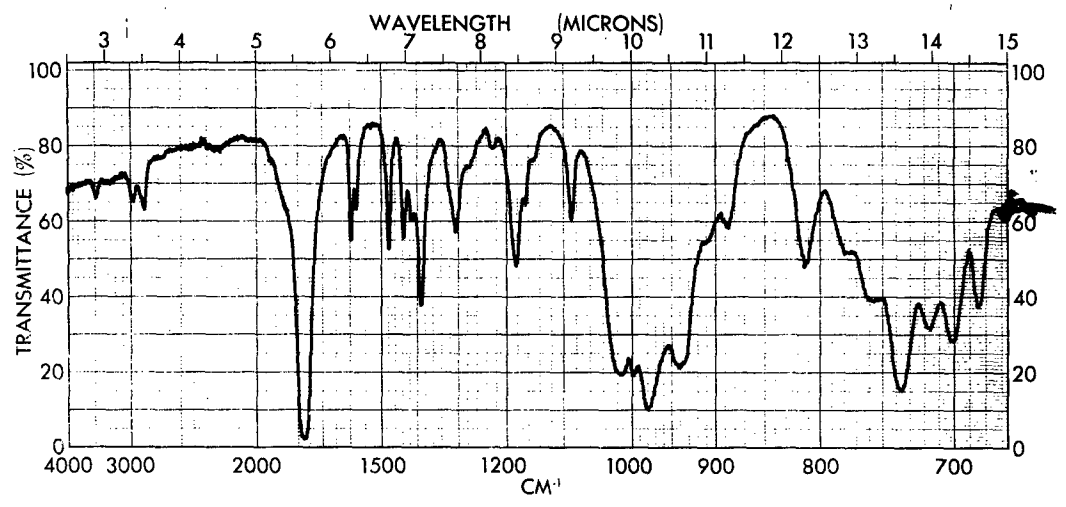


Figure 73 - Infrared Spectrum of m-Phenylenediacetyl Chloride (Liquid)

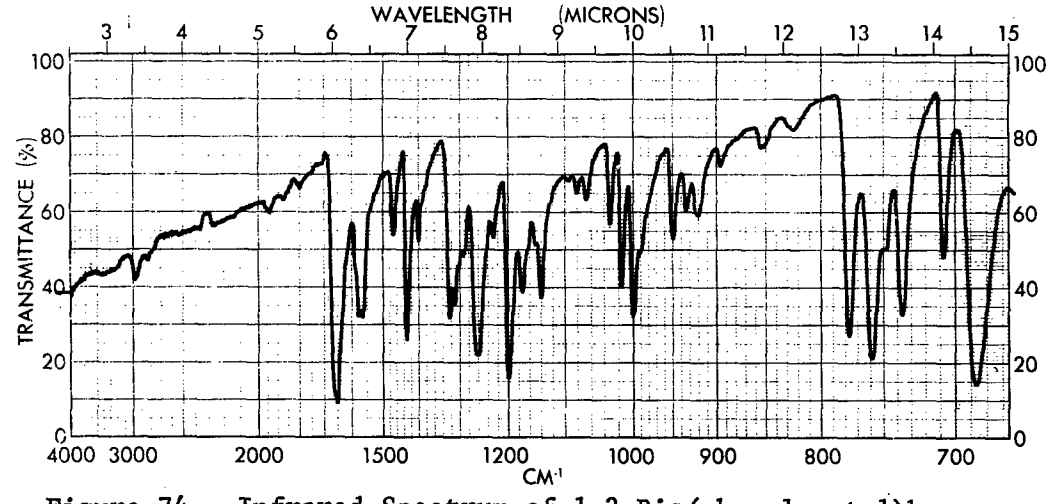


Figure 74 - Infrared Spectrum of 1,3-Bis(phenylacetyl)benzene (KBr)

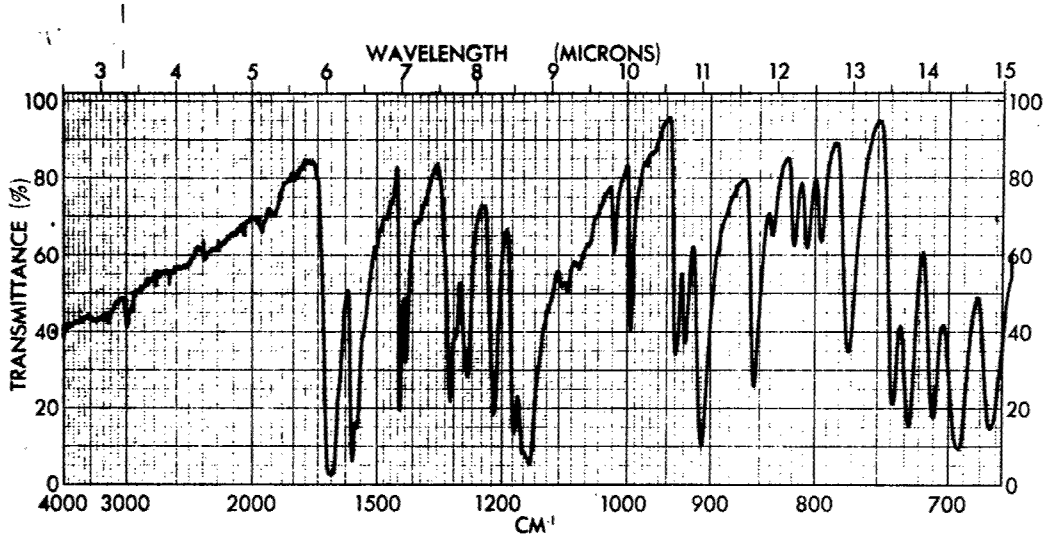


Figure 75 - Infrared Spectrum of 1,3-Bis(phenylglyoxaloyl)benzene (KBr)

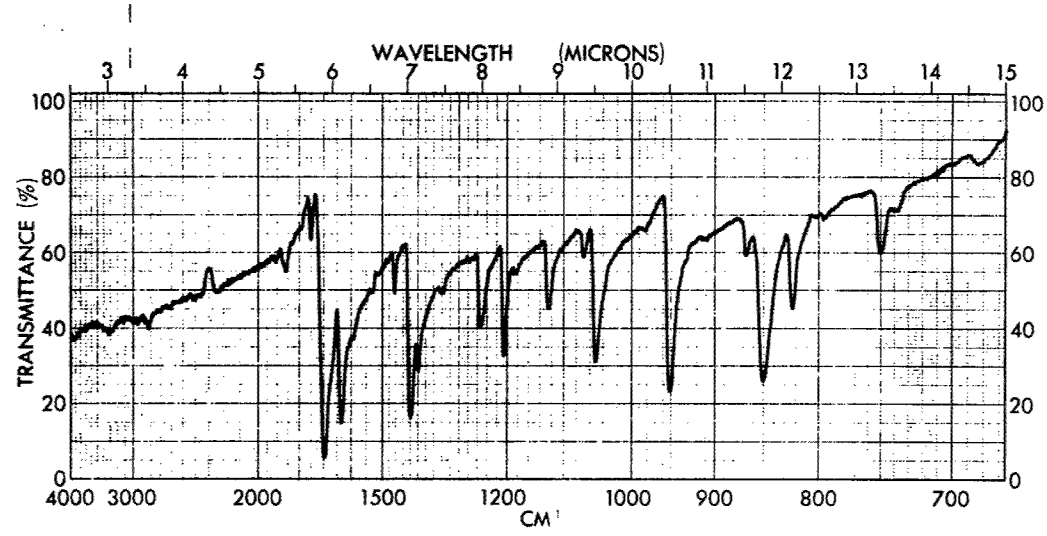


Figure 76 - Infrared Spectrum of Pyracen-1,2-dione (KBr)

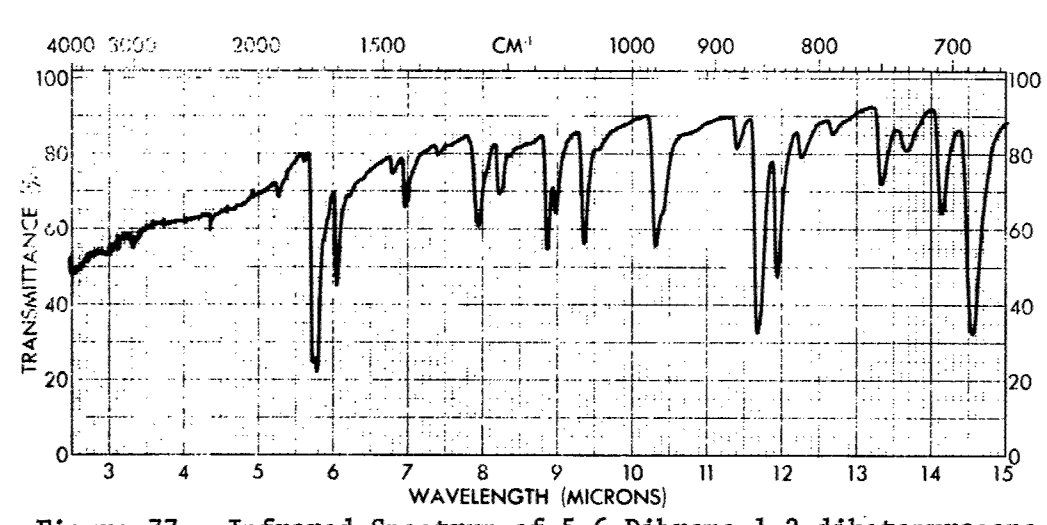


Figure 77 - Infrared Spectrum of 5,6-Dibromo-1,2-diketopyracene (KBr)

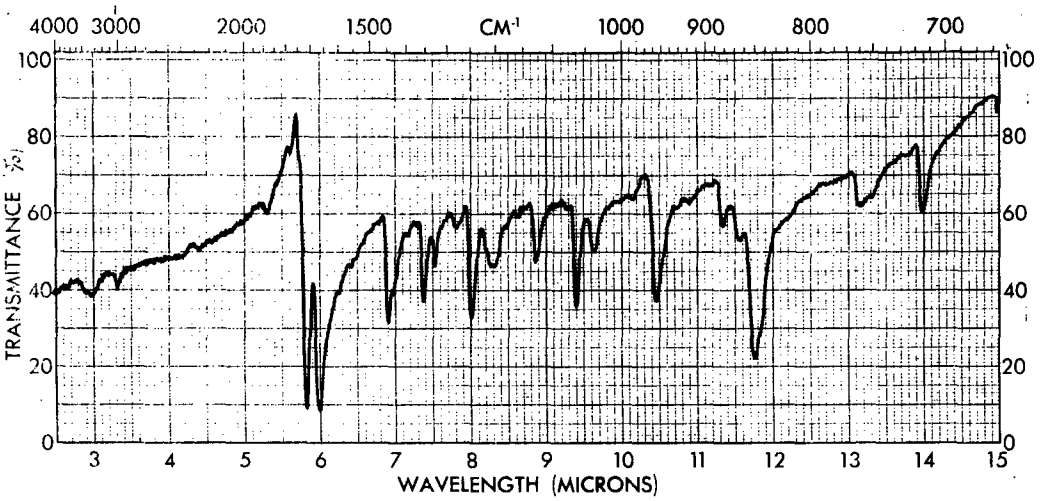


Figure 78 - Infrared Spectrum of Pyracyloquinone (KBr)

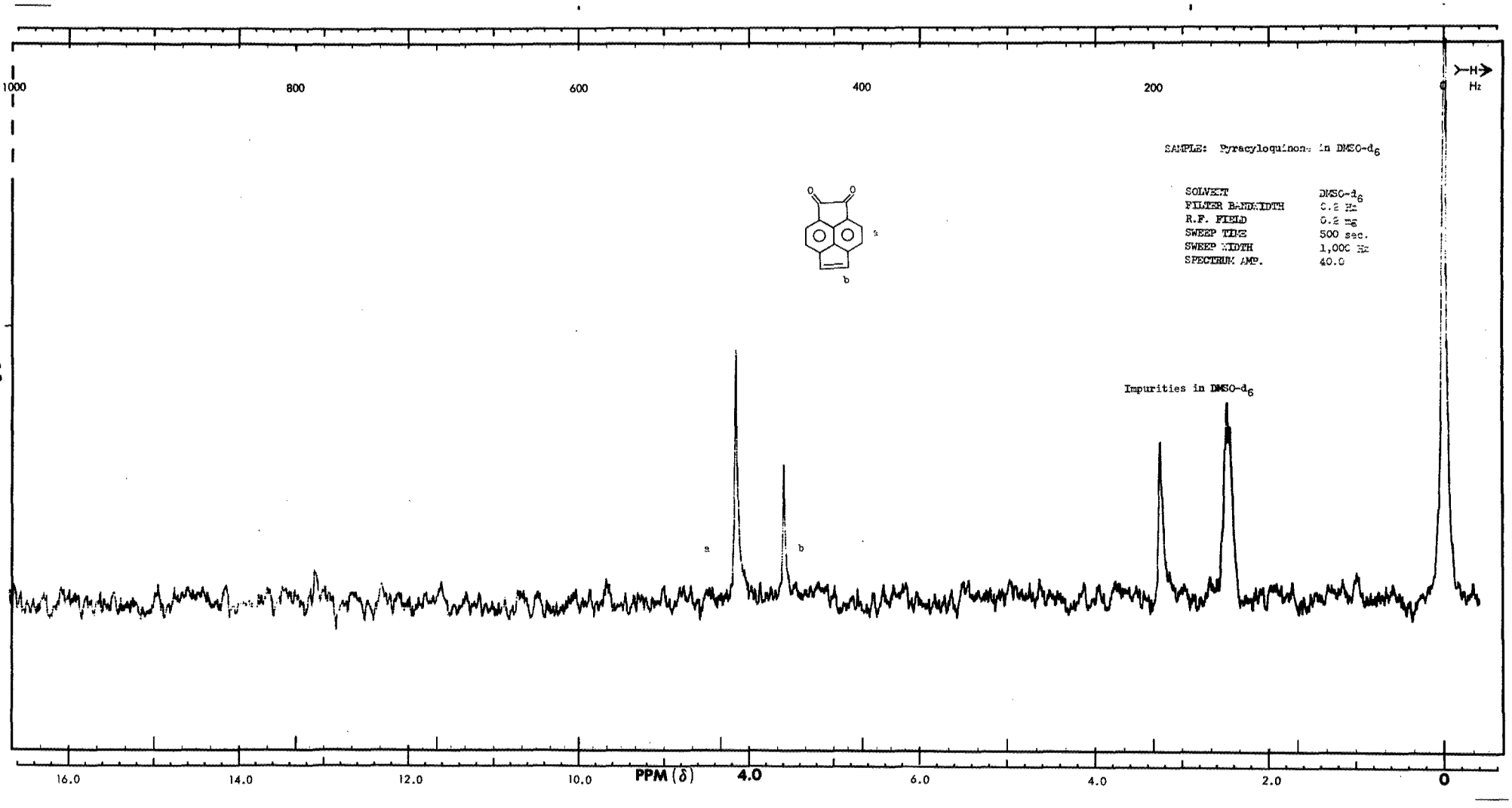


Figure 79 - NMR Spectrum of Pyracyloquinone

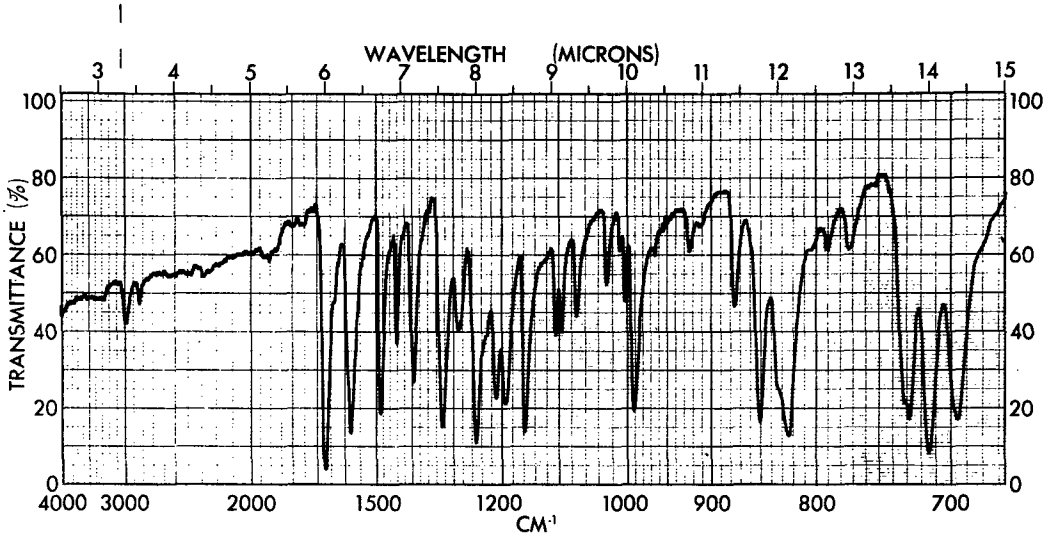


Figure 80 - Infrared Spectrum of p,p'-Di(phenylacetylphenyl)ether (KBr)

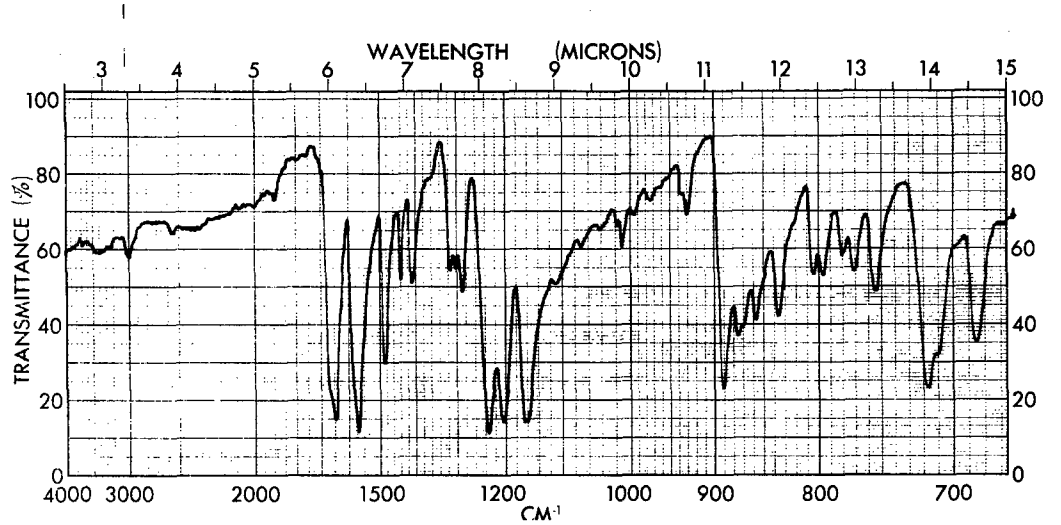


Figure 81 - Infrared Spectrum of p,p'-Oxydibenzil (KBr)

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13. ABSTRACT

Work on the synthesis of the following substances is reported: Benzidine 3,3'-dicarboxylic acid, 6,6'-bis-([4H],3,1-benzoxazine-2,4-[1H]dione), diethyl 2,5-diaminoterephthalate, pentafluorophenylphosphonous dibromide, bis(pentafluorophenyl)-phosphinous bromide, perfluoro-1-bromo-4-n-octylbenzene, 1,1'-bis(formyl)ferrocene, 1,3-bis(phenylglyoxaloyl) benzene, pyracyloquinone, and p,p'-oxydibenzil. Work on the characterization of the following compounds is reported: 1,1'-bis(formyl) ferrocene, ruthenocene, hexabromobenzene and hydroxymethylferrocene. The purification of 1,4,5,8-naphthalenetetracarboxylic acid and 1,4,5,8-naphthalenetetracarboxylic 1:8,4:5-dianhydride, and the preparation of poly[(7-oxo-7H,10H-benz[de]-imidazo[4',5':5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL polymer) is also reported.

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Monomers						
Synthetic Methods						
Metallocenes						
Perfluoroaromatics						
Multifunctional Aromatics						
Organophosphorous Compounds						
BBL Polymer						
1,4,5,8-Naphthalenetetracarboxylic Acid						